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WOODHOUSEITE, A NEW MINERAL OF THE BEUDANTITE GROUP

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Summary of Properties

Formula: $2CaO \cdot 3Al_2O_3 \cdot P_2O_5 \cdot 2SO_3 \cdot 6H_2O$.
Crystal system: hexagonal (rhombohedral subsystem).
Axial ratio: $a:c = 1:1.170$ ($\alpha = 91°42'$).
Sp. gr.: 3.012.
H.: $4\frac{1}{2}$.
Color: colorless to flesh-colored; transparent or translucent.
Luster: vitreous; pearly on $c\{0001\}$ and cleavage.
Cleavage: excellent basal (0001).
Optical character: uniaxial positive; also biaxial.
Indices: $n_\gamma(\epsilon) = 1.647$, $n_\alpha(\omega) = 1.636$ (± 0.003).
Birefringence: $n_\gamma(\epsilon) - n_\alpha(\omega) = 0.011$.

Woodhouseite is a new sulfate-phosphate member of the beudantite group. It is found in small quantities in quartz veins that adjoin and penetrate the commercial andalusite deposits[1] located on the west slope of White Mountain in the Northern Inyo Range, Mono County, California. The andalusite deposits occur in pre-Cambrian meta-quartzite,[2] and have been formed by intrusion of late Jurassic granitic rocks that are offshoots of the Inyo Batholith.

The name woodhouseite is proposed in honor of Mr. C. D. Woodhouse, General Manager, Champion Sillimanite, Inc., and well known as an enthusiastic and able mineral collector.

Physical Properties

Woodhouseite occurs in euhedral crystals which are colorless and transparent, or may be white or flesh-colored and translucent. Luster is vitreous, but is pearly on $c\{0001\}$. The specific gravity has been determined to be 3.012 at room temperature by the pycnometer method, 3.580 grams of material being used. Cleavage is excellent in one direction parallel to $c\{0001\}$.

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[1] Kerr, P. F., The occurrence of andalusite and related minerals at White Mountain, California: *Econ. Geol.*, vol. **27**, pp. 614–642, 1932.

[2] Lemmon, Dwight M., Geology of the andalusite deposits in the Northern Inyo Range, California: *Ph.D. Dissertation, Stanford University,* **1937**.

The optical character is uniaxial positive, but basal sections of the larger, striated crystals are composed of six radial biaxial segments, sixty degrees apart. The centers of some of these crystals are uniaxial, and cleavage fragments of small, undistorted crystals appear uniaxial. The axial angle 2V is about 20° maximum, and the axial plane is oriented in each segment approximately at right angles to the adjoining edge of the hexagonal crystal outline (average measured angle is 87°). Similar anomalies have been noted for certain other members of the alunite-beudantite group.

The birefringence of woodhouseite is 0.011, measured in oriented thin section by comparing the interference color with that of quartz mounted in the same section. Indices of refraction are

$$n_\alpha=1.636, \quad n_\beta=1.638, \quad n_\gamma=1.647 \quad (\pm 0.003).$$

Determination of n_α and n_γ has been made by the oil-immersion method using an E-22 filter, fragments that are completely dark between crossed nicols being used to find n_α. The third index, n_β, has been estimated from the interference colors in an oriented thin section that gives a biaxial figure. The biaxial segments are not completely dark between crossed nicols, but give gray interference colors; a zonal banding is sometimes shown, different bands showing slightly different colors.

GEOMETRICAL CRYSTALLOGRAPHY

Woodhouseite occurs in rhombohedral crystals of variable habit. The optical characteristics show that the large, striated crystals are only pseudo-rhombohedral. Forms observed are $c\{0001\}=\{111\}$, $r\{10\bar{1}1\}=\{100\}$, $t\{40\bar{4}1\}=\{3\bar{1}\bar{1}\}$, $u\{50\bar{5}1\}=\{11.\bar{4}.\bar{4}\}$, and $s\{02\bar{2}1\}=\{11\bar{1}\}$. Crystal faces are frequently curved, striated, or etched, and give poor reflection signals. Twelve good crystals, ranging in size from $\frac{1}{3}$ mm. to 1 mm. and suitable for measurement, have been discovered after careful search. The acceptable measurements from these crystals are given in Table 1:

TABLE 1

	Number of observations	Measured mean	Calculated	Measured range
cr	32	53°30′	—	53°12′–53°41′
rr′	12	88 18	88°15′	88 09 –88 33
ct	18	79 26	79 31	78 47 –80 11
cu	2	81 35	81 35	81 28 –81 43
cs	3	69 47	69 42	69 09 –70 20

Unreliable reflections have also been observed from the following doubtful forms: $\{10\bar{1}2\}=\{411\}$, $\{30\bar{3}1\}=\{7\bar{2}\bar{2}\}$, $\{50\bar{5}4\}=\{14.\bar{1}.\bar{1}\}$, $\{07\bar{7}4\}=\{11.11.\overline{10}\}$, $\{05\bar{5}2\}=\{77\bar{8}\}$. These doubtful forms have given reflections from line faces in curved portions of a few crystals.

Character of faces. The faces of *c* are commonly rough and pitted because of surface alteration, but are never curved. The faces of *r* are always brilliant, but are frequently striated horizontally and slightly curved. The faces of *t* are usually narrow, and are rarely plane, curvature sometimes extending from *r* through *t* and *u*. The form *u* is not common and its faces are very small. The faces of *s* are small; they are usually dull or pitted and give poor signals, but are present on a number of crystals.

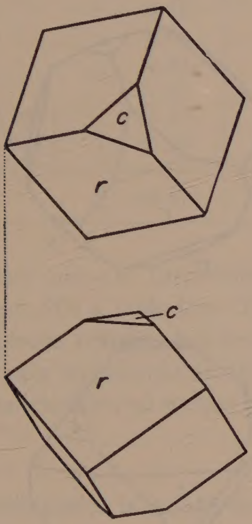

FIG. 1

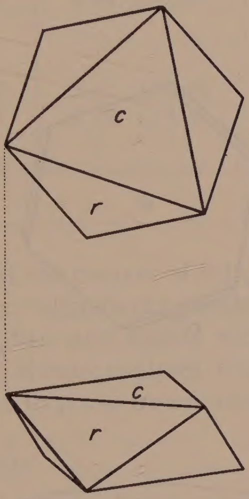

FIG. 2

The faces of the forms *c* and *r* are best developed and give the most reliable signals. The axial ratio $a:c=1:1.170$ ($\alpha=91°42'$) has been calculated from the fundamental measured angle *cr*. Computed values for other interfacial angles, using this ratio, compare favorably with the measured angles, and the best measurements are in close agreement with the axial ratio.

Habit. The commonest habit is pseudo-cubic with the single form $r\{10\bar{1}1\}$; the sides of the largest observed crystals of this type are one centimeter in size, and range downward to one-tenth millimeter or less.

Frequently the basal pinacoid *c* modifies the pseudo-cubic habit (Fig. 1) The modifying rhombohedrons *t*, *u*, and *s* (Fig. 4) occur less commonly, and to casual inspection simulate faces of a hexagonal prism, a form that has not been identified upon measured crystals. Equal development of *c* and *r* results in wedge shaped crystals (Fig. 2). Very thin plates (Fig. 3) caused by the dominance of *c* have been found in a few specimens; the maximum diameter of these platy crystals is about five millimeters. Similar crystal habits and forms have been described for various other members of the alunite-beudantite group.

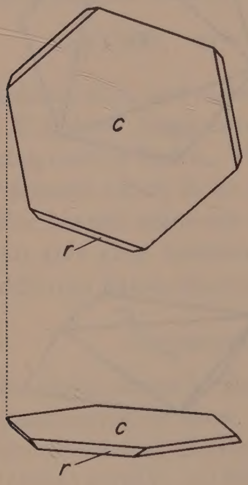

Fig. 3

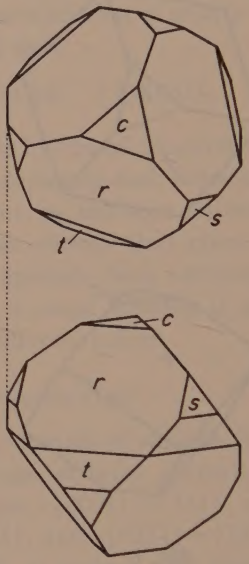

Fig. 4

Chemical Composition

Woodhouseite is readily soluble in dilute acid after it has been heated in a closed tube to drive off the water. Calcium sulfate hemihydrate crystallizes from the HCl solution. Qualitative tests for aluminum and phosphate are excellent. The following analysis has been made by Mr. A. Rautenberg, Ceramic Division, Champion Spark Plug Company. The material analyzed consisted of crystals which were pried from vugs in quartz, then crushed to 20–40 mesh and sorted under a binocular microscope to separate all traces of rutile and limonite.

The molecular ratio is in good agreement with the formula $2CaO \cdot 3Al_2O_3 \cdot P_2O_5 \cdot 2SO_3 \cdot 6H_2O$, the theoretical composition of which is shown

TABLE 2. CHEMICAL ANALYSIS OF WOODHOUSEITE

	Analysis	Molecular ratios				Theoretical composition
P_2O_5	18.13%		.1276	1.07	1×1.07	17.15%
SiO_2	0.30		—	—	—	—
Al_2O_3	36.63		.3593	3.00	3×1.00	36.93
CaO	12.31	.2195	.2326	1.94	2×0.97	13.54
SrO	0.25	.0024				—
BaO	1.00	.0065				—
MgO	0.11	.0027				—
Na_2O	0.08	.0013				—
K_2O	0.02	.0002				—
SO_3	17.59		.2197	1.84	2×0.92	19.33
$H_2O+105°C.$	13.25		.7353	6.15	6×1.02	13.05
$H_2O-105°C.$	0.20		—	—	—	—
Total	99.87					100.00

in the last column. Inspection shows that the content of P_2O_5 is a little high, and SO_3 a trifle low. This deviation suggests the possibility of an isomorphous relationship between phosphate and sulfate with the formation of a mixed crystal. In the absence of more analyses, the variation from the theoretical values is insufficient to prove isomorphism.

OCCURRENCE

Woodhouseite is a late hydrothermal mineral lining vugs in quartz veins that cross the andalusite zones. Although not abundant, the mineral has been observed in both the upper and lower andalusite deposits, and appears to be widespread in small amounts. It is commonly associated with topaz, quartz, augelite, lazulite, tourmaline, barite, muscovite, and pyrophyllite, all of which formed previously to it. Small crystals frequently coat euhedral quartz and augelite.* A few interesting specimens have been found showing clear, pseudo-cubic woodhouseite crystals strung like beads upon hair-like crystals of colorless tourmaline (achroite). In the portions of veins that are open to supergene solutions, woodhouseite is usually coated with the supergene minerals jarosite and limonite, and sometimes with hyalite opal.

Woodhouseite is found only near masses of lazulite, which has probably provided some of the chemical components. No quantitative analysis of the lazulite has been made, but qualitative tests indicate the presence of calcium. T. L. Watson[3] has shown that the lazulite from Graves Mountain, Georgia, contains 3% CaO, and notes that lazulite from some other localities contains appreciable amounts of calcium. There are no other abundant calcium-bearing minerals associated with the andalusite deposits, although calcite is a constituent of the adjoining schistose porphyry.

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* The geometrical crystallography of augelite will be described in a later paper.

Strontium-bearing natroalunite, which is also present in the andalusite deposits, is more abundant than woodhouseite. It usually occurs in coarsely granular masses or veins a foot or less in width, accompanied by muscovite and quartz. Small amounts of finely granular natroalunite have attacked the andalusite ores. Euhedral crystals, which are rough and wedge shaped, are not common. Natroalunite and woodhouseite have not been observed together. They can be distinguished by chemical tests, specific gravity, indices of refraction, or crystal habit. The natroalunite has the following properties: specific gravity, 2.90; SrO = 2.81%, $Na_2O:K_2O:SrO = 5:4:3$; $n_\epsilon = 1.608$, $n_\omega = 1.587$ (±0.003).

THE BEUDANTITE GROUP

Woodhouseite belongs to the beudantite group, which includes the isomorphous minerals beudantite, corkite, svanbergite, and hinsdalite. The name of the group is derived from the first known representative, described by A. Levy in 1826, and named in honor of the French mineralogist, F. S. Beudant. Many of our mineral names were first applied by Beudant, who systemized much of the nomenclature.[4]

Properties of the members of the isomorphous group are compared in the following table, which includes chemical composition, axial ratio, rhombohedral angle α (for the three-axis method), specific gravity, and indices of refraction.

TABLE 3

		c	α	*Sp. gr.*	*Indices*	
					ω	ε
Beudantite	$2PbO \cdot 3Fe_2O_3 \cdot As_2O_5 \cdot 2SO_3 \cdot 6H_2O$	1.184	91°16′	4.1±	1.96	B.=mod.
Corkite	$2PbO \cdot 3Fe_2O_3 \cdot P_2O_5 \cdot 2SO_3 \cdot 6H_2O$			4.2±	1.93	B.=low
Woodhouseite	$2CaO \cdot 3Al_2O_3 \cdot P_2O_5 \cdot 2SO_3 \cdot 6H_2O$	1.170	91 42	3.01	1.636	1.647
Svanbergite	$2SrO \cdot 3Al_2O_3 \cdot P_2O_5 \cdot 2SO_3 \cdot 6H_2O$	1.206	90 34	3.30	1.626	1.640
Hinsdalite	$2PbO \cdot 3Al_2O_3 \cdot P_2O_5 \cdot 2SO_3 \cdot 6H_2O$	1.268	88 39	3.65	1.671	1.689

The optical properties for the four previously known members of the

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[3] Watson, T. L., Lazulite of Graves Mountain, Georgia, with notes on other occurrences in the United States: *Jour. Wash. Acad. Sci.*, vol. **11**, no. 16, pp. 386–391, 1921.

[4] Beudant, F. S., *Traité élémentaire de minéralogie.* Paris, **1824:** 2nd. ed., 2 vols., **1832.**

group have been taken from Larsen and Berman.[5] The iron members, beudantite and corkite, are optically negative; the aluminum members, positive. All members of the group, with the exception of svanbergite, which has not been investigated, show an anomalous biaxial character, basal sections being composed of six biaxial segments. The crystallographic axial ratio for beudantite and corkite is a combined average, necessitated by failure of early investigators to distinguish between the two minerals.[6] The axial ratio for hinsdalite[7] was computed from measurements made with a contact goniometer.

Svanbergite was first described as a calcium aluminum sulfate-phosphate (1854). G. T. Prior[8] proved that strontium, not calcium, was the dominant alkaline earth metal present in the original material. The only satisfactory complete analysis of svanbergite, in which the strontium was also erroneously given as calcium, was made for C. W. Blomstrand (1868) upon lead-bearing svanbergite (3.82% PbO) from Westanå, Sweden.

The following mineral associations have been observed for various members of the beudantite group:

Beudantite: quartz, bindheimite, mimetite, carminite, pyrolusite, limonite.
Corkite: pyromorphite, limonite.
Hinsdalite: quartz, barite, pyrite, galena, tetrahedrite, rhodochrosite.
Svanbergite: kyanite, lazulite, pyrophyllite, mica, quartz, hematite, rutile, augelite.

The mineral association reported for svanbergite is similar to that for woodhouseite. The members of the beudantite group have been formed by late hydrothermal solutions or by oxidation wherever they are found.

THE ALUNITE-BEUDANTITE GROUP

G. T. Prior noted the close relationship of the beudantite group to the goyazite (hamlinite) group and to the alunite group. Later, W. T. Schaller[9] discussed the three groups as subdivisions of a major alunite-beudantite group, and, taking alunite, goyazite, and corkite as type examples, showed the following chemical analogy:

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[5] Larsen, E. S., and Berman, H., *The Microscopic Determination of the Nonopaque Minerals*, 2nd edition: *U. S. Geol. Surv., Bull.* **848,** p. 219, 1934.

[6] Hintze, C., *Handbuch d. Mineralogie*, 46 lief., p. 724, **1931.**

[7] Larsen, E. S., and Schaller, W. T., Hinsdalite, a new mineral: *Am. Jour. Sci.*, 4th ser., vol. **32,** p. 251, 1911.

[8] Prior, G. T., Hamlinite, florencite, plumbogummite, beudantite, and svanbergite as members of a natural group of minerals: *Mineral. Mag.*, vol. **12,** pp. 249–254, 1900.

[9] Schaller, W. T., The alunite-beudantite group: *U. S. Geol. Surv., Bull.* **509,** pp. 70–76, 1912.

Alunite	$K_2O \cdot 3Al_2O_3 \cdot 4SO_3 \cdot 6H_2O$	*or*	$[Al(OH)_2]_6 \cdot [K_2] \cdot [SO_4]_2 \cdot [SO_4]_2$
Goyazite	$2SrO \cdot 3Al_2O_3 \cdot 2P_2O_5 \cdot 7H_2O$	*or*	$[Al(OH)_2]_6 \cdot [Sr] \cdot [HPO_4]_2 \cdot [Sr(PO_4)_2]$
Corkite	$2PbO \cdot 3Fe_2O_3 \cdot 2SO_3 \cdot P_2O_5 \cdot 6H_2O$	*or*	$[Fe(OH)_2]_6 \cdot [Pb] \cdot [SO_4]_2 \cdot [Pb(PO_4)_2]$

S. B. Hendricks[10] has obtained x-ray data for alunite, jarosite, natrojarosite, argentojarosite, ammoniojarosite, plumbojarosite, goyazite (hamlinite), karphosiderite, borgströmite, and the artificial compound $3Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$. He has derived the crystal structure from this study. The space lattice is rhombohedral; so three axes of reference should be used instead of four. X-ray data for karphosiderite, borgströmite, and goyazite (hamlinite) were obtained from material that had not been analyzed, and lattice dimensions were not determined. No mineral of the beudantite group was investigated.

Hendricks offers an explanation of the various types of isomorphous replacements on the basis of his structure determinations. The simple replacements include Na^+, K^+, Rb^+, Ag^+, NH_4^+; Ca^{++}, Ba^{++}, Sr^{++}, Pb^{++}; Al^{+++}, Fe^{+++}; and PO_4^{---}, AsO_4^{---}. In plumbojarosite, half the potassium atoms of jarosite are replaced by lead atoms, the other half of the positions remaining vacant, and the rest of the structure is practically undisturbed. In minerals of the beudantite group, this vacant position is filled by R″ atoms, and SO_4 is replaced by PO_4 or AsO_4. Replacements involving change in charge (e.g., Sr^{++} for K^+, or PO_4^{---} for SO_4^{--}) are balanced by corresponding replacement of an oppositely charged ion or by replacement of R^+ or OH^- by H_2O neutral. Schaller's concept of HPO_4^{--} replacing SO_4^{--} is abandoned.

The well-established members of the three allied mineral groups as they are now known consist of the minerals tabulated below. The year first described, the name, the chemical composition, the axial ratio c, and the rhombohedral angle α (for the three-axis method) are listed. The formulae are patterned upon those proposed by Hendricks.

Alunite Group

1824	Alunite	$K\ Al_3\ (SO_4)\ (SO_4)\ (OH)_5\ (OH)$	1.252	89°10′
1902	Natroalunite	$Na\ Al_3\ (SO_4)\ (SO_4)\ (OH)_5\ (OH)$	—	—
1852	Jarosite	$K\ Fe_3\ (SO_4)\ (SO_4)\ (OH)_5\ (OH)$	1.249	89 15
1902	Natrojarosite	$Na\ Fe_3\ (SO_4)\ (SO_4)\ (OH)_5\ (OH)$	1.104	93 50
1927	Ammoniojarosite	$NH_4\ Fe_3\ (SO_4)\ (SO_4)\ (OH)_5\ (OH)$	1.18*	91 25
1923	Argentojarosite	$Ag\ Fe_3\ (SO_4)\ (SO_4)\ (OH)_5\ (OH)$	1.106	93 42
1902	Plumbojarosite	$Pb\ [Fe_3\ (SO_4)\ (SO_4)\ (OH)_5\ (OH)]_2$	1.216	90 18

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[10] Hendricks, S. B., The crystal structure of alunite and the jarosites: *Am. Mineral.*, vol. **22**, pp. 773–784, 1937.

Beudantite Group

1826	Beudantite	Pb	Fe_3	(SO_4)	(AsO_4)	$(OH)_5$	(OH)	1.184	91 16
1869	Corkite	Pb	Fe_3	(SO_4)	(PO_4)	$(OH)_5$	(OH)		
1937	Woodhouseite	Ca	Al_3	(SO_4)	(PO_4)	$(OH)_5$	(OH)	1.170	91 42
1854	Svanbergite	Sr	Al_3	(SO_4)	(PO_4)	$(OH)_5$	(OH)	1.206	90 34
1911	Hinsdalite	Pb	Al_3	(SO_4)	(PO_4)	$(OH)_5$	(OH)	1.268	88 39

Goyazite (Hamlinite) Group

1884	Goyazite								
(1890	Hamlinite)	Sr	Al_3	(PO_4)	(PO_4)	$(OH)_5$	H_2O	1.185	91 15
1786	Plumbogummite	Pb	Al_3	(PO_4)	(PO_4)	$(OH)_5$	H_2O	—	—
1906	Gorceixite	Ba	Al_3	(PO_4)	(PO_4)	$(OH)_5$	H_2O	—	—
1902	Florencite	Ce	Al_3	(PO_4)	(PO_4)	$(OH)_5$	(OH)	1.190	91 04

* *X*-ray measurement by S. B. Hendricks.

The new minerals argentojarosite, ammoniojarosite, and woodhouseite have been added to those listed by Schaller (quoted by Hendricks), and the doubtful minerals karphosiderite and harttite have been omitted.

Karphosiderite was accepted by Schaller to include a number of similar or identical hydrous ferric sulfates with the probable composition $3Fe_2O_3 \cdot 4SO_3 \cdot 7H_2O$, analogous to jarosite. Many specimens of karphosiderite have been shown to be mixtures. The mineral borgströmite, which is probably identical with the artificial compound $3Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$ (or $H_2OFe_3(SO_4)_2(OH)_5H_2O$), may be a distinct mineral, or may possibly belong under the name karphosiderite. The status of the natural hydrous ferric sulfates remains undecided.

More information is required to establish harttite as a definite mineral. The name is based on a chemical analysis of a somewhat impure aggregate found in the Brazilian phosphate favas. Schaller interpreted the same analysis as an isomorphous mixture of about two parts of goyazite (hamlinite) with one part of strontium-alunite.

Schaller showed the probable identity of hamlinite and goyazite, and later acknowledged that goyazite has priority.[11]

The fact that more of the theoretically possible members of these three mineral groups have not been identified is probably explained by the difficulty of obtaining sufficiently pure material in large enough quantity for investigation. The lack of material also explains the missing data for many of the established minerals. Measurable euhedral crystals have never been found for natroalunite, ammoniojarosite, plumbogummite, gorceixite, or harttite. Mixed crystals have been observed within limits, but the rarity of occurrences has prohibited discovery of many intermediate members, or in some cases of end members. The alunite-natroalunite series is most thoroughly known, although pure natroalunite has not yet been found.

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[11] Loughlin, G. F., and Schaller, W. T., Crandallite, a new mineral: *Am. Jour. Sci.*, 4th series, vol. **43**, p. 69. 1917.

ACKNOWLEDGMENTS

The writer is deeply indebted to Professor A. F. Rogers for suggestions and for criticism. Dr. J. A. Jeffery, Vice-President, Champion Spark Plug Company, has furnished the chemical analysis, which was made by Mr. A. Rautenberg. Mr. C. D. Woodhouse has permitted free use of material from his collection.

MUTUAL INTERFERENCE IN THE MICROCHEMICAL DETERMINATION OF ORE MINERALS

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Introduction

The use of microchemical methods is spreading rapidly, both for the qualitative and quantitative determination of elements. Microchemistry offers a decided advantage over "bulk" methods, not only because of the greater speed with which the determinations can be carried out, but also because of the very small amounts of material required for a test. Microchemical methods are particularly valuable in determining the composition of the small inclusions in ores and metallurgical products.

Most of the reagents used are sufficiently sensitive to show the presence of 0.005 per cent or less of the desired element. Needless to say, if such minute quantities of an element are to be identified, it is essential that the procedure of the test be carefully followed and the utmost caution taken that there is no pollution of the reagent or the test drop. Despite such care, it frequently happens that the test obtained is not wholly satisfactory. Either the color of the precipitate is unusual, the form is changed or entirely different, or sometimes no test is obtained when previous observations have indicated that the element should be present. When such changes occur—and they occur frequently, even in the hands of skilled technicians—the observer is never certain whether they are due to variations in the p_H of the solution, concentration of reagent or solution, or to the presence of some interfering anion or cation. The first two variables can be controlled by proper attention to the procedure of the test; in many cases the last variable—presence of an interfering anion or cation—is beyond control. Often, much time could be saved by recognizing that a given variation in the precipitate is caused by the presence of another element. In fact, some of the interferences are as characteristic of the interfering element as any other known test.

The presence of a variety of elements in the test drop is due either to a poor sample or to a complex mineral. A poor sample is obtained if the original area of the mineral or inclusion is too small. In this case, allowance can usually be made for the presence in the solution of elements of the host mineral, although their presence may cause notable interferences. Where the mineral varies in composition there may be no hint of the presence of elements, other than those expected in the mineral, until trouble is encountered in the testing.

The sulphide minerals are notoriously impure; in fact, the use of microchemistry has been responsible in considerable part for the recognition of the extent of isomorphic replacement. Sometimes the presence of these "impurities" is unimportant and can safely be ignored, particularly among the more complex sulphide salts. Many times microchemistry is employed, not to determine the major constituents, but to determine the presence of small amounts of other elements replacing the major constituents in the mineral. Consequently it is essential to have sensitive tests and also to know the limitations of these tests.

It might be possible to devise two tests for every element. One test would be sensitive only to large amounts of the element, and would serve to indicate those elements present in amounts sufficient to enter into the formula of the mineral. The other test might be very sensitive and serve to show small amounts of the element present as "impurities." Such a system, however, would involve the use of many more reagents, more time in testing, and would inevitably fail in border line cases. Moreover, the same results can be obtained by controlling the concentration of the test drop, and using a sensitive precipitant.

Very little attention has been given in the literature of microchemistry to the effect of the presence of other elements on the nature of the precipitate for any particular test. Some reference to the interference of particular elements on some tests are to be found scattered through the publications of Short,[1] and of Chamot and Mason,[2] but the list is far from complete. It is the purpose of this paper to collect and check all interferences that have been previously described and in addition to describe hitherto undescribed interferences in the standard microchemical tests for the twenty most common elements of the metallic minerals. Suggestions are made for circumventing some of the difficulties occasioned by these interferences.

Not all of these twenty elements can interfere in each of the tests studied. Some of them are stable only in nitric acid, some only in hydrochloric acid, and others are stable in both acids. Likewise the reagents investigated require either a nitric, hydrochloric, neutral, or alkaline solution to produce satisfactory precipitation. All of the twenty elements stable in that solution are considered as potential interfering elements. No elements are excluded from investigation because they are not known to occur together in a mineral. As far as the authors are aware, no mineral containing gold and cadmium is known at present, but that does not mean that one may not be found in the future, or that gold may not occur in such minute disseminations in a cadmium mineral as to be inseparable by mechanical means. Moreover, it is hoped that the results of this study may be of value in fields other than mineralogy, in which event there might be no limitation to the association of the elements.

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[1] Short, M. N., Microscopic Determination of the Ore Minerals: *U. S. Geol. Survey, Bull.* **825**, 1931.

[2] Chamot, E. M., and Mason, C. W., Handbook of Chemical Microscopy, Vol. II: Wiley and Sons, New York, **1931**.

The present scheme for the systematic testing of a mineral by microchemical methods—as outlined in *U. S. Geol. Survey, Bull.* **825**—has been in use for several years and gives satisfactory results for most ore minerals. The purpose of the present work is to increase the usefulness of that scheme by pointing out some of the pitfalls for the unwary and by clarifying interpretation of the results under particular circumstances. Under certain conditions, mentioned later, the tests recommended in that procedure are misleading or entirely unsatisfactory. Resort may then be made to other tests or to a different procedure. This study brings out the need for alternate tests for some of the elements which seriously interfere and commonly occur together.

The authors are indebted to Professor M. N. Short, of the University of Arizona, for the use of his lists of the reactions of individual elements with several of the reagents. Descriptions of some of these reactions have been modified by the authors, who performed the tests under somewhat different conditions. Professor A. O. Beckman of the California Institute has given the authors much valuable advice concerning possible chemical explanations of some of the interference reactions noted. Mr. M. H. Evans, California Institute, discovered and studied the thiourea test for selenium, and the authors acknowledge his kindness in permitting its inclusion in this paper.

Procedure

For each of the twenty elements studied a solution containing 1 per cent of the metallic ion (not of the salt from which the ion was derived) was prepared in either 1 per cent HNO_3 or 1:5 HCl as indicated below, except the nitric solutions of tellurium, selenium and bismuth. The standard solution of tellurium was 0.1 per cent in 10 per cent nitric acid, of selenium was 1 per cent in 5 per cent nitric, and of bismuth was 1 per cent in 10 per cent nitric. The use of the elements in acids of the aforementioned concentrations closely simulates the actual conditions under which the tests give the most satisfactory results. A part of these standard solutions was then diluted to give a 0.1 per cent or a 0.01 per cent solution of the element. Each element for which the test can be used was tried in the presence of as many of the remaining twenty ions listed below as were stable under the conditions of the test.

TABLE 1. ELEMENTS INVESTIGATED

Element stable in 1 per cent HNO_3	Element stable in 17 per cent HCl	Element stable in both 1 per cent HNO_3 and 17 per cent HCl	
Cd ++	Sb +++	As +++	Hg ++
Pb ++	Au +++	Bi +++	Ni ++
Ag +	Sn ++++	Co ++	Se
Te	Ti +++	Cu ++	Zn ++
		Cr +++	Cl −
		Fe +++	NO_3 −
		Mn ++	SO_4 −−

Two distinct conditions were recognized in making the tests: first, where only one of the cations (positive metallic ions) gave a useful test with the particular reagent (thus, the thiocyanate test for iron in the presence of manganese); secondly, where both cations gave a useful test with the particular reagent (thus, the thiocyanate test for iron in the presence of copper).

When only one of the cations gave a useful test, a 0.1 per cent solution of the reacting cation was first tested in the presence of a 1 per cent solution of the other ion. If no reaction was obtained, a 1 per cent solution of the reacting cation was tested in the presence of a 1 per cent solution of the other ion. If still no reaction was obtained, a 1 per cent solution of the reacting cation was tested in the presence of a 0.1 per cent solution of the interfering ion. This method gives a range of concentration of 100 per cent. In some tests, the solution strengths were 1, 0.1 and 0.01 per cent. Different concentrations of anions were used. These concentrations will be mentioned later.

Where both metals gave a useful reaction with the particular reagent, a 0.1 per cent solution of the first ion was run in the presence of a 1 per cent solution of the second ion. Then a 0.1 per cent solution of the second ion was run in the presence of a 1 per cent solution of the first ion. Where either or both of these groupings did not give the desired reactions for both elements, the reaction was run with both metals present in a 1 per cent solution.

In the interference reactions described throughout the paper, *the list* gives only the *lowest relative proportion of the interfering element* which will cause interference, except in special instances specifically mentioned. Thus, when a 1 per cent cobalt solution is described as interfering with a 1 per cent cadmium solution in the thiocyanate test, it is to be assumed, unless otherwise stated, that a 1 per cent cobalt solution will likewise interfere with a 0.1 per cent cadmium solution, but that a 0.1 per cent cobalt solution will not interfere with a 1 per cent cadmium solution.

Each reaction was watched throughout the period of evaporation until the reagent began to precipitate out from the drop. In a climate where the humidity is not extremely low, this procedure often entails a relatively large expenditure of time, but, in the presence of other ions, many of the most useful reactions are much delayed. All extraordinary delays in the reactions are noted in the article, but to consider all delays in the reactions as interferences (within the definition to be given) would be to increase very greatly the already large number of interferences noted. It is, therefore, regarded as advisable to watch the drop throughout the period of evaporation.

"Interference" is used throughout to mean any marked change in size, shape, or color of the precipitate, as well as the rapidity of precipitation. If the precipitate of the interfering element is so bulky or similar to that of the reacting element as to impede the recognition of the test, it would also be classed as an interference. Of course, the size, shape and rapidity of precipitation vary with the relative concentration of the test drop and reagent and consequently comparisons were only made between tests containing the same quantity of the reacting cation. Changes in the color, size or shape of the precipitate which were not great enough to seriously affect the recognition of the test were not considered as interferences. Throughout the work, the tendency was to regard all tests as satisfactory unless there was serious doubt as to the identity of the precipitate.

A "major interference" is one in which the proportion of the interfering ion is equal to or less than the reacting ion. In a "minor interference," the interfering ion is ten times or more abundant than the reacting ion.

For each test studied in detail, the information is presented as follows:

(a) The reaction of each element with the particular reagent.
(b) Where the test is useful for more than one element a chart is given showing the interference phenomena for each element in the presence of each of the possible interfering ions.
(c) A description of each of the interference reactions.
(d) A discussion of the particular test with regard to its value for detecting each metal for which it can be used, together with possible methods for remedying some of the interferences noted.

The tests are taken up in the following order:

1. Ammonium molybdate
2. Potassium mercuric thiocyanate
3. Dimethylglyoxime
4. Ammonium bichromate
5. Cesium chloride
6. Potassium iodide
7. Double iodide
8. Thiourea
9. Sodium bismuthinate.

Symbols

For the sake of brevity a few symbols are used throughout the paper and are here listed:

(C, pp.—)	Interference discussed in whole or in part in Chamot and Mason.[3]
(S, pp.—)	Interference discussed in whole or in part in *Bulletin* **825.**
(W, pp.—)	Spot reaction described by Watson.[4]
O	No mutual interference.
X	Mutual interference—described in text of article.
—	Can not be present in solution together.
+	Not possible to determine the extent to which the cation interferes with the reaction since it is in solution with an interfering anion.
(1)	Concentration in per cent of the element in solution. Thus (1) denotes 1 per cent of the element, (0.1) denotes 0.1 per cent.

1. AMMONIUM MOLYBDATE TEST

Individual Reactions

A drop of the element in 1 per cent nitric acid solution is allowed to partly evaporate and then a drop of the reagent added and the evaporation slowly completed on a warm hot plate. The residue is dissolved in 1:7 HNO_3.

Ag	No precipitate.
As	Lemon yellow octahedra.
Bi	No precipitate.
Cd	No precipitate.
Co	No precipitate.
Cu	No precipitate.
Cr	No precipitate.
Fe	No precipitate.
Hg	On addition of ammonium molybdate a precipitate of small black grains slowly forms. After evaporation and addition of nitric acid, there remains a peripheral deposit of small black cubes, white or faintly yellow in reflected light.
Mn	No precipitate.
Ni	No precipitate.
Pb	On addition of ammonium molybdate a slow precipitation of small black grains occurs. After evaporation and addition of nitric acid, there remains a heavy precipitate of black cubes and grains around edge of drop. These are white in reflected light.

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[3] Chamot, E. M., and Mason, C. W., *op. cit.*

[4] Watson, J. Adam, Colour reactions in the micro-chemical determination of minerals: *Mineral. Mag.*, vol. **24,** pp. 21–34, 1935.

Se	Selenium does not redissolve in nitric acid but remains as a brownish, fine-grained precipitate, white in reflected light.
Te	Tellurium does not redissolve in nitric acid but remains as a fine-grained precipitate of black grains, white in reflected light.
Zn	No precipitate.

Interference Reactions

No interference was noted in the test on a (0.01) arsenic solution in the presence of a (0.1) solution of Ag, Bi, Cd, Co, Cu, Cr, Fe, Mn, Ni, Se, Te, and Zn.

A (1) solution of Hg or Pb does not interfere with the test on a (0.01) As solution except that the Hg and Pb precipitates tend to mask the As test. The color of both the Ag and Pb precipitates is white.

The presence of much HCl or H_2SO_4 in the test drop appears to decompose the ammonium molybdate and ruin the test.

2. POTASSIUM MERCURIC THIOCYANATE TEST

Individual Reactions

A drop of a (3) solution of the reagent is merged with a drop of the element in (1) HNO_3 where possible, otherwise in the solution previously mentioned. All reactions occur in a (0.1) solution of the element unless otherwise stated.

Sb	No precipitate.
As	Gray, peripheral, amorphous precipitate. Good colorless, hexagonal plates are formed in a (1) solution. Precipitate very slow in forming.
Bi	No precipitate.
Cd	Blunt, white prisms which usually have cavities at each end. Reaction delayed in a (0.1) solution.
Co	Blue prisms and spherules.
Cu	Greenish-yellow, moss-like aggregates and prisms.
Cr	No precipitate.
Au	Yellowish-brown, moss-like aggregates, gold colored in reflected light. Not present in (0.1), but present in a (0.3) solution.
Fe	Solution turns red. Rather faint in (0.1).
Pb	White granular amorphous precipitate.
Mn	No precipitate.
Hg	Mercuric ions give no precipitate.
Ni	White to brown spherules. Test delayed in (0.1).
Se	Numerous, peripheral, greenish-yellow globules, very late forming. As drop dries up, elemental selenium is deposited.
Ag	Curdy, white, fine-grained precipitate.
Te	No precipitate.
Sn	No precipitate.
Ti	No precipitate.
Zn	White, feathery crosses.

Interference Chart

Element Tested for	Sb	As	Bi	Cd	Co	Cu	Cr	Au	Fe	Pb	Mn	Hg	Ni	Se	Ag	Te	Sn	Ti	Zn	Cl	SO_4
Cd	+	○	○		×	×	○	+	×	○	○	○	×	○	×	○	+	+	×	×	×
Co	○	○	○	○		×	○	○	×	○	○	○	×	○	○	○	○	○	×	○	○
Cu	○	○	○	○	×		○	×	×	○	○	○	×	○	×	○	×	×	×	○	○
Au	○	○	○	○	○	×	○		○	○	○	○	○	○	○	○	○	○	○	○	○
Fe	○	○	○	○	○	○	○	○		○	○	○	○	○	×	○	○	○	○	○	○
Ni	+	○	○	×	×	×	○	+	○	○	○	○		○	○	○	+	+	○	×	○
Ag	–	○	○	○	○	×	○	–	○	○	○	○	○	○		○	–	–	○	×	○
Zn	+	○	×	×	×	×	○	+	○	○	×	×	×	○	○	○	○	○		×	○

Interference Reactions

Cadmium

Cd (1) Sb (0.1)	No Cd test. Performed in 1:5 HCl.
Cd (1) Co (1)	All crystals colored blue. Cd not easily recognizable.
Cd (0.1) Cu (1)	Poor Cd test.
Cd (1) Cu (1)	Fair Cd test. Many crystals are tapered and colored light green.
Cd (1) Au (1)	No Cd test. Performed in 1:5 HCl.
Cd (1) Fe (1)	Cd test poor and difficultly recognizable.
Cd (1) Fe (0.1)	Good Cd test. Crystals colored light lavender.
Cd (1) Ni (1)	No Cd test.
Cd (1) Ni (0.1)	Cd crystals often tapering and in peripheral clusters.
Cd (0.1) Ag (1)	Ag precipitate masks Cd.
Cd (1) Sn (1)	No Cd test. Performed in 1:5 HCl.
Cd (0.1) Ti (1)	No Cd test. Performed in 1:5 HCl.
Cd (0.1) Zn (1)	No distinguishable Cd test.
Cd (1) Cl (2)	A satisfactory test is not obtained if the chloride ion concentration is much above 2%. Since some of the above ions were used in chloride solution (17%), the presence of the chloride rather than the metallic ion may very probably be the cause of the interference. The above tests would indicate that the mercuric and titanium ions somewhat counteract the effect of the chloride ions.
Cd (0.1) SO_4 (1)	Cd crystals much delayed and very poorly formed. Test only difficultly recognizable.

Cobalt

Co (0.1) Cu (1)	No Co test.
Co (0.1) Fe (1)	All Co crystals dark, irregular, peripheral aggregates. Test poor.
Co (1) Fe (1)	All Co crystals dark, but well formed.
Co (1) Ni (1)	No evidence of Co until evaporation very far advanced and then only blue globules form.
Co (0.1) Zn (1)	No Co crystals, all Zn crystals tinged blue.

Copper

Cu (0.1) Co (1)	Crystals of Cu form, but all colored blue.
Cu (0.1) Au (1)	Good Au test—no Cu test. Au and Cu precipitates can easily be mistaken for one another. Performed in 1:5 HCl.

Cu (0.1) Fe (1)	Many colorless, arrowhead-shaped crystals. No recognizable Cu forms.
Cu (0.1) Ni (1)	Ni spherules are all tinged green—otherwise no Cu test.
Cu (0.1) Ag (1)	Cu largely masked.
Cu (0.1) Sn (1)	No Cu test. Performed in 1:5 HCl.
Cu (0.1) Ti (1)	Cu test not recognizable. Performed in 1:5 HCl.
Cu (0.1) Zn (1)	Zn crystals all tinged purple—otherwise no Cu test.

Gold

Au—Cu	The copper and gold precipitates can be easily confused. The gold dendrites are, however, considerably browner and part of the precipitate shows a gold color in reflected light.

Iron

Fe (0.1) Ag (1)	Ag precipitate colored brown—otherwise no Fe test.

Nickel

Ni (1) Sb (0.1)	No Ni test. Performed in 1:5 HCl.
Ni (1) Cd (1)	No Ni test.
Ni (0.1) Co (1)	No Ni test.
Ni (1) Cu (1)	Ni globules green and easily confused with poorly formed Cu clusters.
Ni (1) Au (1)	No Ni test. Performed in 1:5 HCl.
Ni (1) Sn (1)	No Ni test. Performed in 1:5 HCl.
Ni (1) Ti (1)	No Ni test. Performed in 1:5 HCl.
Ni (1) Cl (10)	No Ni test.
Ni (1) Cl (5)	Good Ni test. The interfering effect of the Cl ion thus begins somewhere between 5 and 10 per cent.

Silver

Ag (0.1) Cu (1)	Ag precipitate masked by Cu.
Ag—Sb, Au, Sn, Ti	These elements were present only in chloride solutions and could thus not be tested in the presence of Ag.
Ag (1) Cl (0.1)	Presence of Cl inhibits the Ag test by precipitating AgCl.

Zinc

Zn (0.1) Sb (1)	Maltese crosses, black squares, some Cd-like crystals and some good Zn crosses. Performed in 1:5 HCl.
Zn (0.1) Bi (1)	Numerous formless, colorless to opaque grains and small stubby Cd-like crystals. Few Zn crosses. Poor test.
Zn (0.1) Cd (1)	No Zn test.
Zn (0.1) Co (1)	No Zn test.
Zn (1) Co (1)	Curved prisms and poorly formed crosses—all blue.
Zn (0.1) Cu (1)	No Zn test.
Zn (1) Cu (1)	Some Zn crosses all dark purple in color.
Zn (0.1) Au (1)	Maltese crosses, black squares, Cd-like crystals. Performed in 1:5 HCl.
Zn (0.1) Mn (1)	Many irregular opaque grains; some good crystals.
Zn (0.1) Hg (1)	Poor test, mainly stubby prisms, also a few good Zn crystals.
Zn (0.1) Ni (1)	No Zn test.

Zn (0.1) Cl (15)	Zinc forms much altered; consist mainly of Maltese crosses, black squares, and many crystals that appear very similar to the Cd crystals with cavities at the ends. Since some of the cations used were present in a (17) HCl solution, the Cl rather than the metallic ion may very probably be the cause of the interference noted. 1:5 HCl does not interfere with the (1) Zn test.
Zn (0.1) Cl (10)	Good Zn test.

Discussion

Cadmium: In testing for cadmium, it is imperative to avoid a high chloride ion concentration in the drop. The numerous interferences of the chloride ion in the thiocyanate test afford a strong argument in favor of first attempting to dissolve a mineral in nitric acid before either hydrochloric acid or aqua regia is used. The major interference of cobalt is relatively unimportant since cobalt and cadmium are not common natural associates. The marked interference of iron (C, p. 128) is, however, quite a serious difficulty in view of the widespread occurrence of iron as a mineral impurity. We know of no remedy for interference by iron. The minor interference of silver is relatively unimportant (C, p. 128). Silver can be removed by potassium bichromate before testing for cadmium.

Cobalt: The major interference of nickel (S, p. 135) and iron (S, p. 136) and the minor interference of zinc can be remedied by the use of the cesium chloride test for cobalt (a new test to be described subsequently). The α nitroso-β naphthol test is not a satisfactory test for cobalt.

Copper: The purple color of zinc crystals in the presence of copper, even when no copper dendrites are formed, is often a satisfactory test for copper and one utilized by Watson as a spot test (W, pp. 25, 26). The major interference by gold can be remedied by use of the cesium chloride test for copper. However, the two cations are not commonly associated in minerals, but if they do occur together they can be separated by dissolving the mineral in nitric acid. The cesium chloride test will likewise remedy the minor interference of nickel and cobalt. When tin and titanium are in solution, the potassium iodide test for copper may be of assistance. Some of these interferences have been mentioned previously: cf. copper in the presence of cobalt (S, p. 136), gold (C, p. 250), and zinc (S, p. 130).

Gold: The copper and gold precipitates can be easily confused. The gold dendrites are, however, considerably browner, and part of the precipitate shows a gold color in reflected light. Where copper is present, pyridine-hydrobromic acid will give a satisfactory gold test (S, p. 154). The minimum sensitivity of the gold test with thiocyanate is 0.3 per cent of the element. The interference tests discussed here were (contrary to general practise) run with a 1 per cent gold solution as a minimum concentration.

Iron: The iron test is highly satisfactory. When silver is present in solution, it should be removed by bichromate before a test is run for iron.

Nickel: A high chloride ion concentration will seriously interfere with the nickel test which, even under ordinary conditions, is somewhat delayed. Minor interference is offered by cadmium, cobalt, and copper. However, by using a modification of the dimethylglyoxime test, nickel can be satisfactorily ascertained in the presence of all of the aforementioned ions (W, p. 32).

Silver: The bichromate test is probably preferable to the thiocyanate test. However, other than the interference of the chloride ion, only copper will offer a minor interference to this test.

Zinc: The presence of a relatively high chloride ion concentration in dilute zinc solutions materially alters the zinc precipitate. Black squares, maltese crosses, and many prisms that are very similar to the cadmium prisms appear. Copper offers a major interference to this test although, even when no zinc crystals are present, the purple color of the copper dendrites may aid in the detection of zinc. There is no present remedy for the major interference of cobalt (S, pp. 131–132). There is likewise no remedy for the minor interference of nickel or cadmium (C, pp. 128–129).

3. DIMETHYLGLYOXIME TEST

Individual Reactions

A drop of reagent is added to a drop containing a (1) solution of the element in neutral or weakly alkaline solution.

Ag	No precipitate.
As	A 1 per cent solution of NH_4OH precipitates much of the arsenic as colorless octahedrons.
Bi	No precipitate.
Cd	No precipitate.
Co	No precipitate.
Cu	No precipitate in 1 per cent nitric acid solution. In 1 per cent ammonia, a strong, yellow fine-grained precipitate of grains and needles forms.
Cr	Yellowish-brown fine-grained precipitate. No precipitate in 1 per cent nitric solution.
Fe	No precipitate on adding a drop of 1 per cent NH_4OH to the iron in 1 per cent or less nitric acid. Color of drop turns brown. No precipitate on addition of dimethylglyoxime.
Hg	Precipitate of very small black grains. White in reflected light.
Mn	No precipitate.
Ni	Immediate precipitation of small pink needles.

Pb	Strong precipitate of very small black grains. White in reflected light.
Se	No precipitate.
Te	On addition of 1 per cent NH_4OH gives a brown to black precipitate. No precipitate from a 1 per cent nitric solution.
Zn	On addition of 1 per cent NH_4OH gives a whitish precipitate. No precipitate in 1 per cent nitric solution.

Interference Reactions

(Test performed by mixing solutions in dilute nitric acid, neutralizing with NH_4OH and adding reagent.)

Nickel

Co (0.1) Ni (0.01)	Presence of Co greatly delays Ni test which appears in small quantities at edge of drop as it dries. Volume of Ni precipitate is greatly lessened. Some check tests gave yellow and purple needles instead of usual red. Test not reliable.
Co (1) Ni (0.01)	Sometimes a trace of nickel; sometimes no nickel test.
Fe (1) Ni (0.01)	No interference if sufficient ammonia has been added to make test drop weakly alkaline.
Hg (0.1) Ni (0.01)	Good precipitate, but needles are colored yellow to purple.
Mn (0.1) Ni (0.01)	Good precipitate but needles colored light yellowish-pink.
Mn (1) Ni (0.01)	Copious precipitate colored yellow to pinkish-brown. Definite color interference.
Pb (1) Ni (0.01)	No interference if solution is weakly alkaline except that lead precipitate of black grains tends to mask the nickel.
Zn (1) Ni (0.01)	No interference if solution is weakly alkaline except that whitish precipitate of Zn tends to mask Ni precipitate.

DISCUSSION

Minor interferences are due to Co, Hg, and Mn. Cobalt interferes (S, p. 134) seriously when it is present in amounts greater than ten times the nickel. There is no easy satisfactory method of separating the two. The presence of either mercury or manganese changes the color of the precipitate but does not prevent its formation. No interference was noted in the presence of As, Ag, Bi, Cd, Cr, Cu, Fe, Pb, Se, Te, Cl, or SO_4.

4. AMMONIUM BICHROMATE TEST

Individual Reactions

Small grains of ammonium bichromate are dissolved in distilled water until the solution is strong enough to give a good test when added to a drop of (0.1) Ag in 1 per cent nitric acid. This solution is then used to test a 1 per cent solution of the elements in 1 per cent nitric acid.

Ag	Yellow blades of silver chromate and red blades of silver bichromate.
As	Slow formation of good octahedrons and tetrahedrons. Some colorless, some dark.
Bi	Immediate fine-grained dark precipitate, green in reflected light. This precipitate is soluble in 1:7 nitric acid and does not reform until the drop dries to give a yellow mass, yellowish-green in reflected light.

Cd	No precipitate.
Cu	No precipitate.
Cr	No precipitate.
Fe	No precipitate.
Hg	Slow precipitation of a few black grains, yellowish-white in reflected light.
Mn	No precipitate.
Ni	No precipitate.
Pb	Immediate precipitation of fine-grained, yellowish grains, yellow in reflected light.
Se	No precipitation until drop begins to dry, then there is a very fine-grained, dark precipitate around edge of drop.
Te	Immediate fine-grained, dark precipitate.
Zn	No precipitate.

Interference Reactions

Silver

As (1) Ag (1)	Slow formation of good octahedrons and tetrahedrons, colorless to dark in transmitted light, white in reflected light. No silver bichromate or chromate blades.
As (1) Ag (0.1)	Octahedrons and tetrahedrons—no silver test.
As (0.1) Ag (1)	Strong silver test.
As (0.1) Ag (0.1)	Slow formation of bladed and feathery forms at edge of drop, dark red to black color. Forms sometimes very feathery.
Bi (1) Ag (0.1)	Immediate fine-grained precipitate soluble in 1:7 HNO_3, good silver test.
Cu (1) Ag (0.1)	Silver blades are small and often colored blue, but test is satisfactory.
Cr (1) Ag (0.1)	Silver blades are stumpy and often form as rounded grains. Test recognizable but not very satisfactory.
Hg (1) Ag (0.1)	Black grains, yellowish-white in reflected light, just before drop dries a few silver bichromate blades may form on edge of drop.
Hg (1) Ag (1)	Good silver test although first formed blades are dark red to black. Precipitate contains numerous black grains also.
Hg (0.1) Ag (0.1)	Irregular grains with a few small blades formed at edge of drop as it dries. Blades are dark red to black in color, red in reflected light.
Pb (1) Ag (0.1)	Heavy yellow lead precipitate partly masks later silver test.
Pb (0.1) Ag (0.1)	Immediate precipitation of lead chromate, later good silver precipitate.
Se (1) Ag (0.1)	Immediate fine-grained precipitate, no silver test.
Se (1) Ag (1)	Black grains, clumps of needles, crosses, white in reflected light. Later, a few red spherules are formed. No silver blades.
Se (0.1) Ag (0.1)	Black grains and needles, then red grains and spherules around edge of drop. No silver bichromate blades.
Se (0.1) Ag (1)	Black grains, colorless to black feathery blades, feathery clumps and crosses; later, formation of blades that are red when they begin to form, but turn black as they grow.
Te (0.1) Ag (0.1)	Fine-grained precipitate. Weak silver test of red to black blades.
Te (0.1) Ag (1)	Fine-grained precipitate, then good silver test.

DISCUSSION

Major interferences by arsenic and selenium occur. In practise, the interference by arsenic is important; that by selenium not important because selenium is ordinarily not readily soluble in weak nitric acid.

Arsenic can be removed by ammonium molybdate. Chlorine is a major interference that must be avoided.

Minor interferences (Bi, Cu, Cr, Hg, Pb, and Te) are relatively unimportant because in each case it is possible to obtain a silver test, although the appearance of the precipitate will be greatly delayed and may differ considerably both in form and color. Where the presence in considerable amounts of any of these elements is suspected, the test drop must be observed until it dries, and any precipitate interpreted in view of the above notes. No interference was noted in the presence of Cd, Co, Fe, Mn, Ni, and Zn. Interference by Mn, Pb, and Hg are mentioned by Chamot and Mason (C, p. 338), and those of sulphuric, selenious and tellurious acids and Pb by Short (S, p. 149).

5. Cesium Chloride Test

Individual Reactions

The reagent is applied in solid form to a drop of the element in 1:5 HCl where possible, otherwise in the solution previously mentioned.

Sb	White hexagons and stars.
As	Numerous, small, formless, late-forming peripheral grains and hexagonal plates.
Bi	Very thin colorless rhombs and knife-like prisms.
Cd	Tiny, colorless, hexagonal bipyramids.
Co	Light blue blades and prisms form around the periphery of the drop very late in the period of evaporation.
Cu	Golden yellow needles appear at edge of drop after evaporation is somewhat advanced. Long brown needles, red under crossed nicols, are also characteristic.
Cr	No precipitate.
Au	Small brown to opaque octahedra, as well as yellowish green, rectangular, anisotropic crystals.
Fe	Bright yellow blades and pyramids which appear anisotropic.
Pb	Small, colorless rhombs, crosses and plates of irregular shape with high refractive index and low double refraction. Precipitate appears in a (0.1) Pb solution from which some Pb has first been precipitated by HCl.
Mn	Colorless, highly refracting prisms and blades often in clusters. Does not form in a (0.1) solution.
Hg	Highly refracting, colorless cubes and octahedra as well as hexagonal plates and prisms with low order interference colors. Does not appear in (0.1) solution.
Ni	No precipitate.
Se	Colorless plates and formless grains. Weak in (0.1) solution.
Ag	Not soluble in a HCl solution, hence no precipitate.
Te	Honey-yellow isometric crystals, chiefly octahedra. Also hexagonal and triangular plates.
Sn	Small white octahedra and Y-shaped crystals.
Ti	Round, colorless, very late forming gray globules. Not formed in a (0.1) solution.
Zn	Colorless rhombs, branching forms, prisms and hexagonal plates showing low order interference colors form at edge of drop. Reaction very much delayed in a (0.1) solution.

Interference Chart

Element Tested for	Interfering Elements																				
	Sb	As	Bi	Cd	Co	Cu	Cr	Au	Fe	Pb	Mn	Hg	Ni	Se	Ag	Te	Sn	Ti	Zn	NO_3	SO_4
Sb		○	○	○	○	×	×	×	○	×	○	×	○	×	–	×	×	×	×	○	○
Bi	○	×		×	○	○	○	×	○	○	○	○	○	○	–	○	○	○	○	○	○
Co	○	○	○	○		×	○	○	○	○	○	○	○	○	–	○	○	○	○	○	○
Cu	○	○	×	○	○		○	○	×	○	×	×	○	×	–	○	×	×	×	×	×
Te	×	×	○	×	○	○	○	×	×	○	○	×	○	○	–		×	○	○	○	○
Sn	○	○	○	×	○	×	○	×	○	○	×	×	○	×	–	×		○	○	○	○

Interference Reactions

Antimony

Sb (0.1) Cu (1)	No Sb test.
Sb (0.1) Cr (1)	Crystallization much delayed. Crystals very irregular and generally unrecognizable.
Sb (0.1) Au (1)	No Sb test.
Sb (1) Au (1)	Sb crystals largely masked by Au and considerably darkened.
Sb (0.1) Pb (1)	No Sb test.
Sb (0.1) Hg (1)	Numerous long peripheral needles and smaller clusters of needles within the drop—all colorless and having weak birefringence. Many small Sb plates largely masked.
Sb (0.1) Se (1)	Crystallization much delayed. Test largely masked.
Sb (0.1) Te (0.1)	Sb crystals very small and indistinct.
Sb (0.1) Sn (1)	Sb masked by Sn precipitate.
Sb (0.1) Ti (1)	Very poor test—very few good Sb crystals.
Sb (0.1) Zn (1)	Sb weak and much delayed.

Bismuth

Bi (0.1) As (1)	Bi largely masked by As.
Bi (0.1) Cd (1)	Bi largely masked by Cd.
Bi (0.1) Au (1)	Bi slow in forming and considerably masked by Au.

Cobalt

Co (1) Cu (1)	Residue colored light green by Cu so that Co can not be recognized.

Copper

Cu (0.1) Bi (1)	No satisfactory Cu test.
Cu (0.1) Fe (1)	Cu precipitate largely masked by Fe precipitate.
Cu (0.1) Mn (1)	No Mn test.
Cu (1) Mn (1)	No good Cu test. Numerous colorless and brown needles.
Cu (0.1) Hg (1)	Hg crystals assume greenish color, but typical Cu needles absent.
Cu (0.1) Se (1)	Crystals of Se colored green, but no other Cu test.
Cu (0.1, 1) Sn (1)	No customary Cu test but peripheral clusters of long, colorless needles as well as the regular Sn test.
Cu (0.1) Ti (1)	No satisfactory Cu test.
Cu (0.1) Zn (1)	No satisfactory Zn test.

Cu (0.1) NO_3 (1)	Cu test much delayed.
Cu (0.1) SO_4 (1)	Many bright yellow hexagonal plates, a few greenish yellow crystals, but no long brown needles.

Tellurium

Te (0.1) Sb (1)	Te precipitate largely masked by Sb.
Te (0.1) As (1)	Te precipitate largely masked by As.
Te (0.1) Cd (1)	No Te test.
Te (0.1) Au (1)	No Te test.
Te (0.1) Au (0.1)	Te present, but largely masked by Au precipitate.
Te—Fe	The Te test is easily confused with the Fe precipitate although it is sometimes possible to distinguish the two.
Te (0.1) Hg (1)	Hg precipitate apparently masks Te. No Te visible.
Te (0.1) Sn (1)	No Te test discernible.

Tin

Sn—Cd	The Cd and Sn precipitates are very similar, but can be distinguished by the anisotropism of the Cd bipyramids as compared to the isotropic Sn octahedra.
Sn (0.1) Cu (1)	No Sn test.
Sn (0.1) Au (1)	Sn largely masked by Au precipitate.
Sn (1) Au (1)	Sn present, but crystals are colored brown and are only difficultly distinguishable from the Au precipitate. The Sn octahedra are generally somewhat smaller than those of the gold precipitate and are not so highly refracting.
Sn (0.1) Mn (1)	Sn crystals small and somewhat delayed.
Sn (0.1) Hg (1)	Sn crystals much delayed and extremely small.
Sn (0.1) Se (1)	Sn apparently forms readily in the presence of Se, but where Sn concentration is low, the Sn precipitate appears similar to the Se with which it might then be confused.
Sn (0.1) Te (0.1)	Sn precipitate poor.

Discussion

Antimony: The major interference to this test is offered by gold. Where the antimony concentration is rather high, the phosphomolybdic acid spot test has been found to be satisfactory (W, p. 29). Antimony and gold are not, however, natural associates. Moreover, if the mineral is decomposed with nitric acid and then leached with cold 1:5 HCl, virtually no gold will be present in the solution. Of the elements that show minor interference, the double iodide test will remedy the effect of zinc, tellurium, chromium, lead, titanium and mercury. The only remedy that can be offered for the interference of copper, selenium and tin is the phosphomolybdic acid test, providing the antimony concentration is sufficiently high.

Bismuth: Major interference to this test is likewise offered by gold, if present. Where the concentration of bismuth is sufficiently high, the thiourea spot test (W, p. 30) is a satisfactory substitute test, although selenium will partly interfere. Minor interference in the chloride test is shown by cadmium and arsenic. Bismuth is not a naturally occurring associate of the former; when the two are present in solution the double iodide test will be satisfactory. The interference of arsenic is more serious and one for which no remedy can be offered, where the arsenic can not be first removed by precipitation with ammonium molybdate.

Cobalt: This test for cobalt has not been previously described. It consists of the formation of blue cobaltous chloride crystals when the evaporation of the drop is well advanced. Only copper, which gives a green residue when the evaporation of the drop is well advanced, will interfere with the test. No remedy can be offered for the copper interference, since copper will likewise interfere with the thiocyanate test. A test that does not appear until the reagent begins to precipitate by evaporation is not, in general, regarded as a useful test. The presence of cobalt is, however, so easily recognized by the use of this test that it is believed that this test will be quite convenient where the thiocyanate test proves unsatisfactory.

Copper: Major interference by tin and manganese characterizes this test. The manganese interference is of no importance since it will not interfere with the thiocyanate test. When tin is present, the only possibility of obtaining a sure copper test is with potassium iodide, a test which is not highly distinctive. Of the ions that offer minor interference, those of sulphate, nitrate, and ferric are most likely to cause trouble. However, neither these three ions nor selenium and bismuth will interfere with the thiocyanate test. When zinc and titanium are present in solution, only the potassium iodide test will be positive.

Tellurium: The fact that iron offers a major interference to this test is indeed a very serious objection to the continued use of cesium chloride test for tellurium. The authors have tried several other tests for tellurium, but none have proved wholly satisfactory. Gold also presents a major interference, but this is unlikely to be important in testing minerals. The telluride minerals are decomposed by nitric acid with liberation of the gold as metallic particles. Leaching the residue dissolves the tellurium, thus separating it from the gold which is insoluble in 1:5 HCl. The solution will give a satisfactory test for tellurium with cesium chloride. The fact that tellurium and cadmium are not common associates makes the major interference of that element unimportant. In the presence of either cadmium or iron, the somewhat indistinctive potassium iodide test for tellurium is satisfactory. The potassium iodide test may also be used when antimony, tin, arsenic and mercury are in solution and would interfere with the cesium chloride test.

Tin: Although no remedy can be offered for the interference of any of the ions, only the interference of copper is of great importance.

6. Potassium Iodide Test

Individual Reactions

The reagent is applied in solid form to a drop of the element in 1:5 HCl unless otherwise noted.

Sb	Solution turns yellow. Color very faint in (0.1).
As	Yellowish green amorphous precipitate. Concentrated solutions give small disks. Reaction delayed in (0.1).
Bi	Addition of KI to a (1) nitric acid solution of Bi yields an immediate, dark, fine-grained precipitate that spreads as a ring from the KI grain, leaving a golden yellow solution. The precipitate is readily soluble in excess KI. Tests performed in HCl give a yellow solution but no precipitate.
Cd	No precipitate.
Co	No precipitate.
Cu	Light yellow amorphous precipitate.
Cr	No precipitate.
Au	Yellow amorphous ring surrounds KI fragment. Ring widens as KI dissolves. Liquid inside of ring colors yellow. Reaction resembles that of selenium, but precipitate is a lighter yellow and some metallic gold (gold-colored in reflected light), as well as light green rectangular to irregular plates, is precipitated.
Fe	Solution turns yellow.
Pb	Greenish yellow hexagons.
Mn	No precipitate.
Hg	Small red and orange cubes and dark red, ragged needles. Needles are bright red in reflected light and very soluble in excess KI. Test faint in (0.1) solution.
Ni	No precipitate.
Se	Chocolate-brown amorphous precipitate.
Ag	In HNO_3 solution, Ag gives an amorphous, yellow-brown precipitate which is milky white in reflected light and not soluble in excess KI.
Te	Chocolate-brown precipitate.
Sn	No precipitate.
Ti	No precipitate.
Zn	No precipitate.

Interference Chart

Element Tested for	Interfering Elements																				
	Sb	As	Bi	Cd	Co	Cu	Cr	Au	Fe	Pb	Mn	Hg	Ni	Se	Ag	Te	Sn	Ti	Zn	NO_3	SO_4
As	×		○	○	○	○	○	×	○	○	○	○	○	○	–	○	○	○	○	○	○
Cu	○	○	○	○	○		○	×	○	×	○	○	○	×	–	×	○	○	○	○	○
Pb	–	○	×	○	○	○	○	–	○		○	○	○	○	×	○	–	–	○	○	○
Hg	○	○	○	○	○	○	○	○	○	○	○		○	×	–	○	○	○	○	○	○
Se	○	○	○	○	○	×	○	×	○	○	○	○	○		–	×	○	○	○	○	○
Ti	○	○	○	○	○	×	○	×	○	×	○	○	○	×	–		○	○	○	○	○

Interference Reactions

All of the following interference reactions were made with both elements in a 1:5 HCl solution except those for Pb, in which all the elements were in a (1) nitric acid solution, since the Pb test is normally made in nitric acid.

Arsenic

As (0.1) Sb (1)	Arsenic precipitate alone gives very few discs at this concentration, but in the presence of Sb, the solution is colored yellow and yellow discs appear which are very similar to those formed in the Sb double iodide test.
As (0.1, 1) Au (1)	Au precipitate largely masks As, although As precipitate is present.

Copper

Cu—Au	Very difficult to distinguish the two precipitates, although both are apparently present in all concentrations.
Cu—Pb	Cu cannot be distinguished in the presence of Pb, but may easily be distinguished by reflected light if no Pb is present and also by the fact that the Cu is not soluble in excess KI.
Cu—Se	Very difficult to distinguish the two precipitates although both are apparently present in all concentrations.
Cu—Te	Interference similar to that of Se.

Lead

Pb—Ag	Good Pb precipitate but in plain light the precipitate is indistinguishable from the Ag precipitate. A distinction can be made in reflected light.
Pb (0.1) Bi (1)	Immediate precipitation of black fine-grained aggregate that spreads as a ring from KI grain, with development of golden yellow color in solution inside ring. Precipitate is brown to white in reflected light. No Pb test.
Pb (1) Bi (1)	Immediate black to red precipitate, red to yellow in reflected light. Glistens like Pb in reflected light and a few yellow plates may form but in general there is no satisfactory lead test.

Mercury

Hg (1) Se (1)	Hg precipitate masked by Se precipitate.

Selenium

Se—Cu	Very difficult to distinguish the two precipitates although both are apparently present in all concentrations.
Se—Au	Se and Au precipitates practically indistinguishable except by reflected light.
Se—Te	Se and Te tests are indistinguishable.

Tellurium

Te—Cu	Very difficult to distinguish the two precipitates although both are apparently present in all concentrations.
Te—Au	Te and Au tests are indistinguishable.

Te (0.1) Pb (0.1, 1)	Presence of Te indicated by yellow color of solution and some brown precipitate although the indications might be overlooked.
Te—Se	Te and Se tests are indistinguishable.

DISCUSSION

Arsenic: The use of the ammonium molybdate test for arsenic avoids any interference by gold or antimony. In fact, the ammonium molybdate test is so satisfactory that none other need be considered.

Copper: It is very difficult to distinguish the copper, gold, selenium and tellurium tests with potassium iodide when it is not already known which one of the metals is in solution. Some difficulty will also be experienced in distinguishing the lead and copper tests unless use is made of reflected light. For this reason, whenever lead, selenium, and tellurium are in solution, the thiocyanate test should be used for copper and, when gold is in solution, the cesium chloride test is recommended.

Lead: The common association of silver and lead makes imperative the use of reflected light in the observation of the lead test. Where difficulty is experienced in determining whether the precipitate is silver or lead, the bichromate test for lead may be of assistance. With the bichromate test, lead is precipitated first and may be later masked by the silver precipitate if the latter is present in a sufficiently high concentration.

Bismuth seriously interferes with the KI test for lead (S, p. 144; C, p. 182) since it forms a double iodide which in the presence of lead gives a red to black, complex precipitate. Even a (0.1) solution of Bi is sufficient to mask the Pb precipitate from a (1) solution. Pb and Bi can be separated (S, p. 145) by converting them to chlorides and leaching the dry drop with water. Bi hydrolyzes to the insoluble BiOCl whereas the Pb chloride is soluble and the solution gives a good lead test with KI.

Mercury: Although this test for mercury is not as commonly used as many of the other tests discussed here, it is useful for testing concentrated solutions in which the thiocyanate test is unsatisfactory. The thiocyanate test for mercury is obtained by adding potassium thiocyanate and cobalt nitrate to the mercuric solution and is thus the cobalt test in reverse. Hence the interference effects of the thiocyanate test for mercury are identical with those in the same test for cobalt (see p. 956). The KI test for mercury, however, is so weak in a 0.1 per cent mercuric solution that in making all the interference tests for mercury here discussed, a 1 per cent solution of mercuric ions was used. Like the lead test, the mercuric test is highly soluble in excess potassium iodide and, moreover, according to Chamot and Mason (C, p. 146), is soluble in the presence of excess mercuric ions although, with the concentrations used by the authors, no difficulty was experienced in this latter respect. Only selenium will interfere with the test by masking the mercury precipitate. When selenium is in solution, the thiocyanate test is satisfactory.

Selenium: The difficulty in ascertaining whether the test is that for selenium, gold, copper, or tellurium, has been previously mentioned. When these elements are in solution the thiourea test for selenium is satisfactory. Also the presence of selenium can be often detected by the deposit of metallic selenium (red in reflected light) that often forms when a test drop containing KI dries.

Tellurium: The difficulties mentioned under selenium are likewise applicable here. The presence of lead may be detected in reflected light. The fact that gold offers major interference to both tellurium tests is a very serious objection to the use of either test when gold is unavoidably present. There is, thus, a need for a satisfactory new test for tellurium to be used when gold and tellurium can not be first separated by selective leaching.

7. Double Iodide Test

Individual Reactions

Potassium iodide and then cesium chloride are applied in solid form to a drop containing the element in 1:5 HCl where possible, otherwise in the solution previously mentioned.

Sb	Orange to red hexagons and stars.
As	Brown, amorphous, peripheral precipitate as well as orange to red hexagons; the latter forming slowly in a 0.1 per cent solution.
Bi	Red hexagonal plates—orange-colored when thin.
Cd	Colorless cubes—not in a 0.1 per cent solution.
Co	Blue-green peripheral prisms and rhombs.
Cu	Long, slender, colorless needles appear in addition to the normal potassium iodide and cesium chloride tests.
Cr	No precipitate.
Au	Precipitate same as from cesium chloride and potassium iodide tests alone.
Fe	Precipitate same as from cesium chloride and potassium iodide tests alone, plus (a) long, red to brown needles which are red under crossed nicols, brown to opaque crystals and yellow hexagonal plates all of which (especially the brown needles) tend to give way to (b) peripheral aggregates of splintery, colorless needles.
Pb	In addition to the normal lead iodide test there is precipitated a mat of slender white needles.
Mn	Same as CsCl test. Not present in 0.1 per cent solution.
Hg	Same as normal cesium chloride and potassium iodide tests—very faint in 0.1 per cent solution.
Ni	No precipitate.

Se	Same as normal potassium iodide and cesium chloride tests plus irregular, reddish brown to opaque crystals.
Ag	Not soluble in HCl.
Te	Same as normal KI and CsCl tests.
Sn	Same as CsCl test.
Ti	No precipitate.
Zn	Same as CsCl test.

Interference Chart

Element Tested for	Interfering Elements																				
	Sb	As	Bi	Cd	Co	Cu	Cr	Au	Fe	Pb	Mn	Hg	Ni	Se	Ag	Te	Sn	Ti	Zn	NO_3	SO_4
Sb		×	×	○	○	×	○	×	○	○	○	○	○	×	–	○	×	○	○	○	○
As	×		×	○	○	×	○	×	×	○	○	○	○	×	–	×	○	○	○	○	○
Bi	×	×		○	○	×	○	×	○	○	○	○	○	×	–	×	○	○	○	○	○

Interference Reactions

Antimony

Sb—As	Arsenic gives a precipitate which, in all concentrations, is very much like the Sb precipitate. Arsenic, however, unlike Sb, gives a precipitate after the KI has been added and before the CsCl is added.
Sb—Bi	Except where one of the elements is greatly in excess of the other, Sb and Bi can, in general, be separated. The Bi test is more sensitive.
Sb (0.1) Cu (1)	No Sb test.
Sb (1) Cu (1)	Sb somewhat masked by Cu precipitate.
Sb (0.1) Au (1)	No Sb test.
Sb (0.1) Se (1)	Sb test weak and much delayed.
Sb (0.1) Sn (1)	Sb crystals small, poorly formed and somewhat delayed.

Arsenic

As—Sb	Arsenic gives a precipitate which, in all concentrations, is very much like the Sb precipitate. Arsenic, however, unlike Sb, gives a precipitate after the KI has been added and before the CsCl is added.
As—Bi	It is difficult to distinguish between As and Bi. One means of distinction is by virtue of the fact that Bi merely gives a yellow color whereas As gives a precipitate after the KI has been added and before the CsCl is added.
As (0.1) Cu (1)	Arsenic test masked by Cu.
As (1) Cu (1)	Many As crystals, but many of the crystals are poorly formed and more brown than usual.
As (1) Au (1)	No distinguishable As test.
As (1) Au (0.1)	Faint As test.
As—Fe	When the Fe concentration is relatively high there may be some difficulty experienced in noting As.

As (1) Se (1)	No As test.
As (0.1) Te (0.1)	Many colorless As crystals are visible, but no good coloration is apparent.
	Bismuth
Bi—Sb	Except where one of the elements is greatly in excess of the other, Sb and Bi can, in general, be separated. The Bi test is more sensitive.
Bi—As	It is difficult to distinguish between As and Bi. One possible means of distinction is by virtue of the fact that Bi merely gives a yellow color, whereas As gives a precipitate after KI and before CsCl is added.
Bi (0.1) Cu (1)	Bi largely masked by Cu.
Bi (0.1) Au (1)	Bi masked by Au.
Bi (0.1) Se (1)	No Bi test.
Bi (0.1) Te (1)	Bi masked by Te.

DISCUSSION

Antimony: When arsenic and bismuth are in solution with antimony and the concentration of antimony is sufficiently high (a 0.1 per cent solution gives a very weak test, a 1 per cent solution gives a strong test), the phosphomolybdic acid spot test (W, p. 29) will give a satisfactory test for antimony. The minor interference of copper, gold, selenium, and tin can perhaps be corrected by use of this reagent. Where only copper is present with the antimony, the cesium chloride test for antimony will be satisfactory.

Arsenic: For the major interference of antimony, bismuth, copper, tellurium, selenium and gold, the ammonium molybdate test for arsenic is satisfactory.

Bismuth: When arsenic and antimony are in solution (and selenium is not in solution) and when the concentration of bismuth is sufficiently high (a 0.1 per cent solution gives a good test), the thiourea spot test for bismuth (W, p. 30) will be useful. The major interference of gold can also be remedied by use of this spot test. For the minor interference of copper and tellurium, the cesium chloride test will constitute a satisfactory remedy and the thiourea test is of assistance. When selenium is in solution the cesium chloride test for bismuth can be used if necessary.

8. THIOUREA TEST

Individual Reactions

A drop of a 10 per cent solution of thiourea in distilled water is added to a drop of a 1 per cent solution of the element in 1:5 HCl, unless otherwise stated.

Ag	Reaction in 1 per cent nitric acid. Ag precipitates as a dark ring at junction of drops, soluble in excess of thiourea.
As	No reaction.
Au	No reaction.
Bi	Solution turns canary yellow, no precipitate.
Cd	No reaction.
Co	No reaction.
Cr	Solution turns faint blue color, no precipitate.
Cu	Immediate heavy, dark, fine-grained precipitate, white in reflected light.
Fe	Solution turns faint pink color, no precipitate.
Hg	Immediate precipitate of colorless needles and dark grains.
Mn	No reaction.
Ni	No reaction.
Pb	No reaction.
Sb	Solution turns faint yellow color, no precipitate.
Se	Immediate precipitation of reddish to blue-black small grains that spread as streamers throughout the drop. Brilliant red in reflected light.
Sn	No reaction.
Te	No reaction.
Ti	No reaction.
Zn	No reaction.

Interference Reactions

Bismuth

The interference tests for bismuth were run in a 1 per cent nitric acid solution.

Ag (1) Bi (0.1)	Silver precipitate partly masks Bi color.
Cr (1) Bi (0.1)	Yellow drop slightly greenish.
Fe (1) Bi (0.1)	Yellow drop slightly orange.
Hg (1) Bi (0.1)	Mercury precipitate partly masks Bi color.
Se (1) Bi (0.1)	Bi color not visible unless drop is filtered.

Selenium

Bi (1) Se (0.1)	The strong yellow color of Bi appears first. Se precipitates but color is obscured by the Bi. In strong reflected light the red selenium precipitate is sometimes visible. Test not always satisfactory.
Bi (1) Se (1)	Satisfactory test.
Cu (1) Se (0.1)	Copper precipitate dark in transmitted light; brownish in reflected light, selenium obscured.
Cu (1) Se (1)	Satisfactory selenium test.
Hg (1) Se (0.1)	Heavy Hg precipitate partly obscures red Se precipitate.
Sb (1) Se (0.1)	Part of the Sb may precipitate by hydrolysis and partly obscure the Se precipitate.

DISCUSSION

The thiourea test for bismuth has been mentioned by Watson (W, p. 30); the application of the test to selenium was worked out by Mr. M. H. Evans, California Institute of Technology.

The test for bismuth is carried out in a weak nitric acid solution. The yellow bismuth color is not intense but is evident for bismuth solutions containing down to 0.01 per cent bismuth. The presence of chlorides tends to inhibit the reaction. The following elements give no reaction in nitric acid and do not interfere with the bismuth test: As, Au, Cd, Co, Cu, Mn, Ni, Pb, Sn, Te, Ti, Zn. Antimony is not stable in nitric acid and hence does not interfere.

Copper and mercury offer minor interferences to the selenium test. None of the other elements studied seriously interfere.

9. Sodium Bismuthinate Test for Manganese

A few grains of the reagent are added to a solution of the element in (1) nitric acid.

In a (0.1) solution of manganese, addition of the reagent colored the solution pink.

No color change took place in Ag, As, Au, Bi, Cd, Co, Cu, Cr, Fe, Hg, Ni, Pb, Sb, Se, Sn, Te, Zn.

Interference reactions, using a (1) solution of the above elements and a (0.1) solution of manganese were run. No interferences were found, except that the presence of Se appears to weaken the intensity of the reaction and make it slow in starting.

Summary of Interferences

In Table II, all of the elements are listed that offer major and minor interferences to the tests. Whenever the test drop of necessity contains the chloride anion and its presence alone is known to cause interference, the observed interference may be due either to the chloride anion or the metallic cation. In these doubtful cases the metallic cation is parenthesized. The table is divided into two sections: Section 1 gives the interferences among the twenty elements studied; Section 2 gives the interference among those elements which would probably be in solution in the test drop in important amounts, at the successive steps in the systematic procedure described in *U. S. Geological Survey*, *Bull.* **825.** Hence, Section 2 contains those interferences which will be encountered in routine microchemical testing of minerals. The number of interferences in Section 2 could be further reduced in those tests performed in HCl solution by thorough leaching with nitric acid which would remove those elements soluble in nitric acid. In actual practise such thorough leaching would probably not be done until an interference was observed. Consequently these ions are left in the table.

TABLE II

Reacting Ion	Test Reagent	Interfering Ion			
		Section 1		Section 2	
		Major	Minor	Major	Minor
Ag	Amm. Bichromate	As, Se	Cu, Cr, Hg, Pb, Te	As	Cu, Hg, Pb, Te
	Pot. Merc. Thiocyanate	Cl	Cu		Cu
As	Amm. Molybdate		Cl, Hg, Pb, SO_4		Pb
	Pot. Iodide	Au	Sb		Sb
	Double Iodide	Au, Bi, Cu, Fe, Sb, Se, Te		Bi, Cu, Fe, Sb, Se, Te	
Au	Pot. Merc. Thiocyanate	Cu		Cu	
Bi	Cesium Chloride		As, Cd, Au		As
	Double Iodide	As, Sb	Au, Cu, Se, Te,	As, Sb	Cu, Se, Te
	Thiourea	Sn——	Hg, Se		
Cd	Pot. Merc. Thiocyanate	(Au), Cl, Co, Fe, Ni, (Sb), (Sn)	Ag, Cu, (Ti), Zn, SO_4	Fe	Zn, Cu
Co	Pot. Merc. Thiocyanate	Fe, Ni	Cu, Zn	Fe, Ni	Cu
	Cesium Chloride	Cu		Cu	
Cu	Pot. Merc. Thiocyanate		Ag, (Au), Co, Fe, Ni, Sn, Ti, Zn		Ag, Co, Fe, Ni, Zn
	Cesium Chloride	Mn, Sn	Bi, Fe, Hg, Se, Ti, Zn, NO_3, SO_4	Mn, Sn	Bi, Fe, Se, Zn
	Pot. Iodide	Au, Pb, Se, Te		Se, Te	
Fe	Pot. Merc. Thiocyanate		Ag		Ag
Hg	Pot. Iodide	Se		Se	
Mn	Sodium Bismuthinate		Se		

Table II (*Continued*)

Reacting Ion	Test Reagent	Interfering Ion			
		Section 1		Section 2	
		Major	Minor	Major	Minor
Ni	Dimethylglyoxime		Co, Hg, Mn		Co, Mn
	Pot. Merc. Thiocyanate	(Au), Cd, Cl, Cu, (Sb), (Sn), (Ti)	Co	Cu	Co
Pb	Pot. Iodide	Bi	Ag	Bi	Ag
Sb	Cesium Chloride	Au, Te	Cr, Cu, Hg, Pb, Se, Sn, Ti, Zn	Te	Cu, Hg, Se, Sn, Zn
	Double Iodide	As, Bi, Cu	Au, Se, Sn	As, Bi, Cu	Se, Sn
Se	Pot. Iodide	Au, Cu Te		Cu, Te	
	Thiourea		Cu, Hg		Cu
Sn	Cesium Chloride	Au, Cd, Te	Cu, Hg, Mn, Se		Cu, Mn
Te	Cesium Chloride	Au, Fe	As, Cd, Hg, Sb, Sn	Fe	As, Hg, Sb
	Pot. Iodide	Au, Cu, Pb, Se		Cu, Se	
Zn	Pot. Merc. Thiocyanate	Cl, Co, Cu	(Au), Bi, Cd, Hg, Mn, Si, (Sb)	Cu	Cd, Mn

Conclusions

The series of tests discussed constitutes a large percentage of all the reactions commonly used in the microchemical identification of the ore minerals. It is hoped that the results obtained will show the dangers inherent in the present systematic scheme and also demonstrate the necessity of carrying out similar interference tests on any new reagents proposed for use.

It has already been pointed out that the number of interferences can be materially reduced by selective leaching of the decomposed mineral residue. This method must be applied with caution, however, because many of the metals that are not soluble in large amounts in a given acid are, nevertheless, sufficiently soluble to go into solution in small amounts after repeated leaching, and often only small amounts of a metal are needed to cause serious interference.

All of the foregoing interferences have been ascertained empirically with little regard to the fundamental chemical causes for such reactions. Many of the interference reactions can be satisfactorily explained by known chemical principles. For example, the interference of the chloride ion with the cadmium test is probably due to the reversible reaction whereby cadmium (and many heavy metals) and chloride ions combine to form negatively charged chloride complexes such as $CdCl_4^{-2}$ and $CdCl_6^{-4}$. In many cases the major trend of such reversible reactions is toward the formation of complex ions which will not give the desired precipitate with the reagent. Whether the reversible reaction tends to go in the direction of the complex ions or in the direction of the simple anion and cation, depends largely on the relative concentration of each element in solution. The effect of a variation in concentration is to cause the amount of a given simple ion present in solution to vary within wide limits. What the available concentration of a given simple ion will be in a given solution of known concentration can be ascertained if the ionization constant of the two ions is known. Many such ionization constants have been determined experimentally. It would thus seem that the most logical method to determine elemental interference would be by the use of the ionization constants to determine the availability of the simple reacting ion in each specific case. The facts that (1) the availability of each ion is dependent on concentration; (2) the constants for all common combinations of anions and cations are not known; (3) the use of such constants becomes quite complex when more than two ions are in solution; (4) and in general microchemical work the exact concentration of the test solution is not known, make it considerably more satisfactory to attack the problem empirically.

However, a knowledge of the chemistry of such solubility and ionization factors is often most useful in predicting qualitatively what effect the mutual presence of two elements in solution may have upon the desired reaction. Thus, because the chloride ion tends to form chloride complexes with many of the metals, whereas the nitrate ion does not form nitrate complexes, it is always advisable to attempt first to dissolve a given mineral in nitric acid and carry out the possible tests before the chloride ion is introduced into the solution. However, because of the many uncertainties involved, the most satisfactory method of quantitatively determining interferences is by empirical methods.

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THE SUBSTITUTION OF SiO_4- AND SO_4-GROUPS FOR PO_4-GROUPS IN THE APATITE STRUCTURE; ELLESTADITE, THE END-MEMBER

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INTRODUCTION AND ACKNOWLEDGMENTS

During the course of an extensive structural investigation[1] of the isomorphism of the apatite group, it has become necessary to investigate the substitutions of the sort found in wilkeite. Although this mineral is reported to contain approximately 12 per cent of SO_3, 9 per cent of SiO_2 and only 21 per cent of P_2O_5, it was correctly assigned to the apatite group by Eakle and Rogers (1) on the basis of its crystallographic, physical and optical properties.

For several reasons it seemed desirable to obtain a new analysis of this most unusual mineral from Crestmore, California. Accordingly some material, supposedly wilkeite, was prepared for analysis by separating it from contaminating minerals (idocrase, calcite, wollastonite, diopside, okenite, etc.) through the use of Thoulet's solution, followed by selection under the binocular microscope. Eight grams of this material was furnished to Dr. Ellestad for analysis, but the results of his determinations are quite different from wilkeite. Indeed, the differences between this mineral and wilkeite are so great as to require a new name. The differences may be summarized as follows:

(1) The new mineral very closely approaches an end-member of the apatite group which has not been previously known to exist.

(2) There seem to be no theoretical objections to the existence of the ultimate end-member.

(3) This material contains only about three per cent of P_2O_5, whereas wilkeite contains nearly 21 per cent, according to the original description (1).

The name ellestadite is proposed for the end-member of the apatite group which contains SiO_4- and SO_4-groups substituting for PO_4-groups. Ellestadite is selected in honor of Dr. R. B. Ellestad, of the Laboratory for Rock Analysis, University of Minnesota, in recognition of his invaluable assistance to geologists and mineralogists as an analytical chemist who has devoted much thought and effort to the composition of earth materials.

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[1] The results of this work will appear later.

Three different lots of material from Crestmore, California, were examined in this study, and certain differences were found, as mentioned below. These will be referred to as follows:

I. Pale rose-colored stringers of ellestadite associated with wollastonite, vesuvianite, diopside, etc., $\omega=1.655\pm.002$, $\epsilon=1.650\pm.002$. Kindly furnished by Dr. A. Pabst, of the University of California.

II. Individual crystals and small groups of pale rose-colored wilkeite in a matrix of coarse blue calcite and associated with diopside, $\omega=1.650\pm.002$, $\epsilon=1.646\pm.002$. Obtained from Mr. R. M. Wilke, Palo Alto, California.

III. Lavender-colored stringers of sugary wilkeite in a fine grained matrix of vesuvianite, pale blue calcite, etc., $\omega=1.640\pm.002$, $\epsilon=1.636\pm.002$. Obtained from Ward's Natural Science Establishment, Rochester, New York.

All of these specimens are uniaxial and negative. The specific gravities and the dimensions of the unit cells show considerable differences, but these properties do not necessarily furnish sufficient data by which to identify these minerals. This is true because of the complications introduced by the variability of the fluorine, chlorine and carbon dioxide. However, it was found that the chlorine content increased with the silica content, whereas the fluorine content decreased, and it is believed that the amount of silica present may be the factor controlling the chlorine content. The problem is further complicated by the presence of the voelckerite molecule $(Ca, X)_{10}O_2(PO_4)_6$.[2]

The writer is indebted to Dr. J. W. Gruner for his kind interest in the problems pertaining to the isomorphism of the apatite group and for his many valuable suggestions. He is greatly indebted to Dr. A. Pabst, of the University of California, who furnished material for the analysis, and to Mr. A. S. Dadson, of Toronto, who supplied the analyzed specimen of fluor-apatite which was used as a basis of comparison. Dr. R. B. Ellestad has furnished several analyses which have been extremely valuable in contributing to an understanding of the isomorphism of the minerals of this group. Messrs. E. L. Berg and Lynn Gardiner have also kindly assisted in several instances.

Structural Data

Náray-Szabó (2) and Mehmel (3) have shown that the unit cell of fluor-apatite contains: 10 Ca-ions, 6 P-ions, 24 O-ions and 2 F-ions.

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[2] The formula of voelckerite is advisedly written as $(Ca, X)_{10}O_2(PO_4)_6$ rather than $Ca_{10}O(PO_4)_6$ which is the formula previously suggested (11). Under these circumstances X has a valence greater than two and is usually carbon. This is discussed more fully below.

The positions of these ions are indicated in Fig. 1, in accordance with the parameters given by Mehmel (4).[3] The P-ions lie at the centers of regular tetrahedra, surrounded by four O-ions. In ellestadite, as shown below, nearly all of these P-positions are occupied by S- and Si-ions and these ions also lie at the centers of tetrahedra. In wilkeite II about one-third of the positions contain phosphorus and the other two-thirds contain S- and Si-ions. These substitutions are possible because the radii of these ions are very similar.

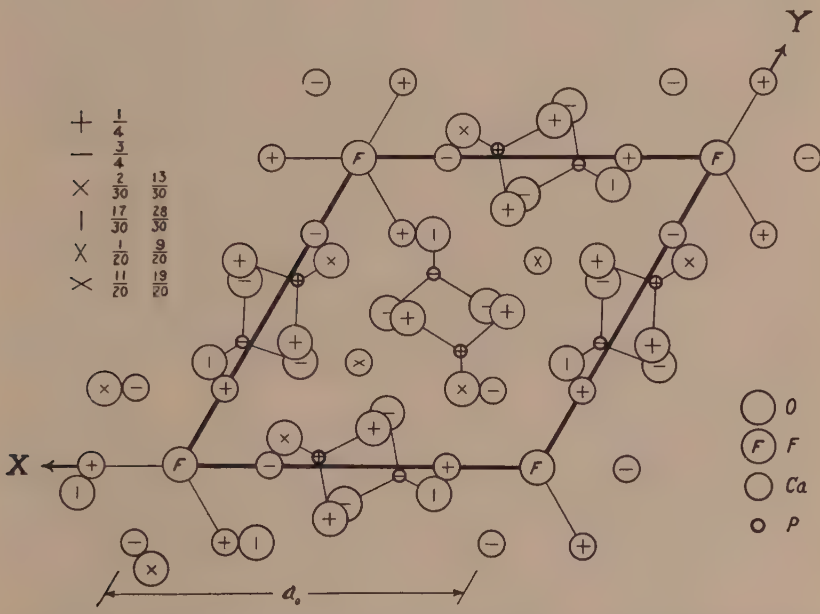

FIG. 1. Projection of the unit cell of fluor-apatite on {0001}. The symbols indicate the distances of the various ions above the base. The F-ions are at $\frac{1}{4}$ and $\frac{3}{4}$ c. The symmetry is $C_{6h}^2 - C6_3/m$.

The interplanar distances obtained for ellestadite are compared with those obtained for fluor-apatite, in Table 1. The fluor-apatite is a specimen from Faraday Township, Hastings County, Ontario, which has been analyzed by Dadson (5, anal. II, p. 59). The unit cell dimensions obtained for ellestadite, wilkeite and fluor-apatite are comparable, as follows:

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[3] Although Fig. 1 is based on the parameters given by Mehmel, it is slightly different from Mehmel's diagram. Why there should be this slight discrepancy is not apparent.

	a_o	c_o	*c/a*	*Vol.*	*Theor. density*	*Meas. density*	P_2O_5 (*wt.* %)
Ellestadite, I	9.53Å	6.91Å	.7251	544	3.046	3.068	3.07
Wilkeite, II	9.48	6.91	.7289	538	—	3.120	14.4
Wilkeite, III	9.40	6.89	.7330	527	—	3.157	32.2
Fluor-apatite	9.36	6.88	.7350	522	3.187[4]	3.18[5]	41.30[6]

(All values for a_o and c_o are ±0.01Å.)

The dimensions obtained for fluor-apatite are quite similar to those obtained by Náray-Szabó, namely, $c_o=9.37$ and $a_o=6.88$ (both ±0.01Å). If these values were determined on analyzed material, this fact was not recorded. It has been found, however, during the measurement of more than twenty specimens of the apatite group, that the differences in the *a*-dimension are considerably greater than those of the *c*-dimension. This is apparent on comparison of ellestadite and wilkeite with fluor-apatite.

The axial ratio obtained by goniometric measurement for wilkeite (1) was .730 and this value is in close agreement with the value obtained by *x*-ray methods (.7289) for specimen II. The slight differences are to be accounted for in terms of chemical differences in the specimens. Contrary to the supposition by Eakle and Rogers (1) wilkeite is *not* nearly constant in composition, but shows considerable variability in the single occurrence at Crestmore.

For reasons which have been fully discussed by Gruner and McConnell (6) in an investigation of carbonate-apatites, it is necessary to assume that the carbon occupies either the P-positions or positions on the threefold axes on which the Ca-ions are located (Fig. 1) or both of these positions. If the carbon occurs on the three fold axes it substitutes for calcium; otherwise it substitutes for phosphorus, but a discussion of these unusual types of substitution cannot be entered into here, and is only mentioned by way of preparing the reader for the disposition which is made of CO_2 in the analysis given below.

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[4] Value calculated from the molecular weight of the theoretical fluor-apatite (1008.9) rather than the constituents reported by Dadson (5, anal. II, p. 59).

[5] This value is preferable to the value (3.176) previously reported (5, p. 59), according to a personal communication from Mr. A. S. Dadson.

[6] This value was actually determined, as compared with 42.27% (for theoretical fluor-apatite), which was used in calculating the theoretical density. This produces a slight discrepancy between the theoretical density and the measured density, because the analysis showed the presence of very small amounts of elements which would tend to decrease the density. Nevertheless, the agreement is excellent, and the use of the constituents actually determined would considerably increase the complexity of the calculations, without furnishing compensating benefits.

TABLE 1. COMPARISON OF POWDER DIAGRAMS OF FLUOR-APATITE AND ELLESTADITE
(Unfiltered Fe Radiation—$r=57.3$ mm.)

		Fluor-apatite		Ellestadite	
No.	Indices	*d*	*I*	*d*	*I*
1	002	3.432	2	3.452	3
2	120, 210	3.060	3	3.118	2
3	300β	2.975	0.5	3.034	0.5
4	202β	2.884	0.5	2.920	0.5
5	121, 211	2.798	>10	2.845	>10
6	112	2.769	4	2.798	4
7	300	2.702	6	2.750	6
8	202	2.616	3	2.647	3
9	301	2.517	0.5	2.557	0.5
10	130β	2.477	0.5	2.523	0.5
11	122, 212	2.289	0.5	2.315	0.5
12	130, 310	2.248	2	2.289	3
13	131, 311	2.135	1	—	—
14	222β			2.161	1
15	113	2.057	1	2.074	0.5
16	123β	2.026	0.5	2.046	0.5
17	203	2.001	0.5	—	—
18	231β	—	—	2.013	0.5
19	222	1.937	4	1.961	6
20	132, 312	1.883	1	1.909	2
21	123, 213	1.838	6	1.857	6
22	231, 321	1.795	3	1.827	3
23	140, 410	1.769	3	1.802	3
24	402	1.745	3	1.771	3
25	004	1.720	3	1.727	3
26	232, 322	1.637	1	1.661	1
27	133, 313	1.605	0.5	—	—
28	240, 420	1.533	0.5	1.560	0.5
29	331	1.521	0.5	1.548	0.5
30	124, 214	1.498	1	1.511	0.5
31	502	1.468	2	1.490	2
32	304	1.452	1	1.464	3
33	233, 323	1.445	1		
34	151, 511	1.424	1	1.451	2

Physical and Optical Data

Although the theoretical density of ellestadite (3.046) does not show particularly close agreement with the measured value (3.068), this discrepancy is no greater than .7 of 1%. Using a fused silica pycnometer (capacity 10 cc.) and a four gram sample, the value obtained was 3.067 (4°C.). Small fragments were used and great care was used to liberate air. An independent determination, using a centrifuge and Thoulet's solution, was made by Mr. E. L. Berg and the value obtained was 3.069 (4°C.). Values for specimens II and III were obtained by the latter method and were, respectively, 3.120 and 3.157. This indicates that the value reported by Eakle and Rogers (1) for wilkeite (3.234) is considerably too high. This value cannot be correct for theoretical reasons because all of the constituents of wilkeite (except manganese, of which 0.77% was reported) are lighter than the corresponding constituents of fluor-apatite. Therefore, the theoretical density cannot be greater than that of fluor-apatite (3.18–3.19), and is probably always considerably less—judging from the specimens examined in this study.

It is noteworthy that the refractive indices decrease with an increase in density in this isomorphous series (Fig. 2). This somewhat unusual relationship obtains because the atomic refractivity of chlorine is much greater than that of fluorine, but chlorine increases the size of the unit cell more rapidly than it increases the molecular weight, thus lowering the density.

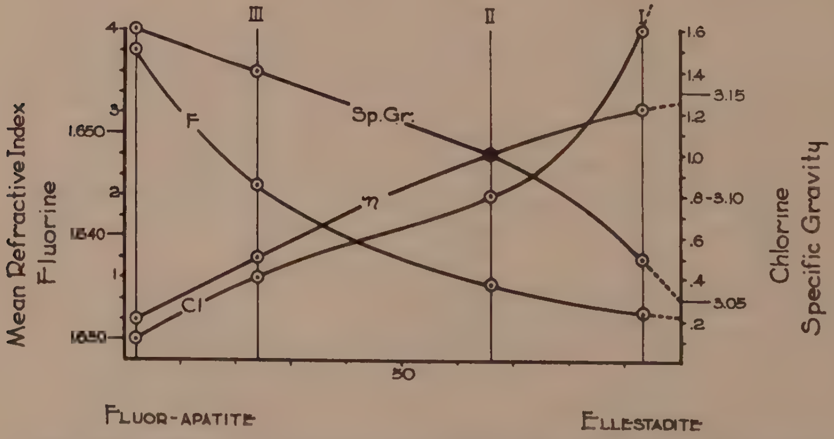

Fig. 2. Comparisons of refringence, specific gravity, chlorine and fluorine for the end-members and two intermediate compounds of the ellestadite-apatite series. The positions of the different members were calculated in terms of the P_2O_5 content, by comparing the amount determined with 42.27% (the theoretical value for fluor-apatite). This approximation is used because the molecular ratio $SO_3:SiO_2$ is not necessarily 1:1, and other complications (oxy-apatite, chlor-apatite, etc.) would make the calculations extremely tedious.

CHEMICAL DATA

An analysis of ellestadite is given in Table 2. The analysis was made on material which was selected as described above. Separate portions were used for P_2O_5 and CaO determinations. The samples were dissolved in HNO_3, and the silica was separated by double evaporation. CaO was determined by the ammonium oxalate-oxalic acid method of Hillebrand and Lundell. P_2O_5 was determined by precipitation as phospho-molybdate, followed by double precipitation as magnesium ammonium phosphate, and ignition to pyrophosphate. A double sodium carbonate fusion, each followed by a water extraction, was used to separate the sulphate from calcium. Silica was removed from this extract by double evaporation from acid solution, and the sulphate was finally precipitated as $BaSO_4$. A sodium carbonate fusion was also made for the chlorine determination. The leached extract from this was acidified with HNO_3, and the chlorine precipitated as AgCl. Fluorine was determined by Armstrong's modification (7) of the method of Willard and Winter (8). Water and carbon dioxide were determined by the usual methods.

TABLE 2. CHEMICAL ANALYSIS AND NUMBER OF IONS IN ELLESTADITE

	1 Wt. %	2 Mol. ratios	3 Ionic ratios	4 Impurities deducted	5 Ionic ratios	6 Number of ions in cell	7 Positive charges	8 Negative charges	9 Molecular weight
CaO	55.18	9.841	9.841	.052	9.789	9.920	19.840		397.49
MgO	0.47	.117	.117	.060	.057	.058	.116		1.41
MnO	0.01	—	—		—	—	—		—
CO_2	0.61	.139	.139		.139	.141	.564		1.69
P_2O_5	3.06	.215	.430		.430	.436	2.180		13.53
SO_3	20.69	2.584	2.584		2.584	2.619	15.714		83.97
SiO_2	17.31	2.882	2.882	.093	2.789	2.826	11.304		79.30
Cl	1.64	.462	.462		.462	.468		.468	16.60
F	0.57	.300	.300		.300	.304		.304	5.78
H_2O+	0.45	.250	.500		.500	.507		.507	8.62
	0.08*	—							
H_2O-	0.10	—							
Fe_2O_3	0.22	.015	.030	.030					
Al_2O_3	0.13	.013	.026	.026					
	100.52				O =	24.721		49.442	395.54
Less O	.61								
	99.91					42.000	49.7	50.7	1003.93

* Removed at 300°C.

In Table 2, column 1 contains the weight per cents of the oxides; column 2 contains the molecular ratios, and column 3 the ionic ratios. Column 5 contains the ratios of the ions after the deduction of the impurities contained in column 4 (see below). Column 6 contains the number of ionic positions relegated to each element; columns 7 and 8 contain the charges of these ions; and column 9 contains the molecular weight.

Although great care was used in selecting the specimen for analysis, it was not possible to obtain material which was entirely uncontaminated. For this reason the deductions shown in column 4 (Table 2) were made because both the original material and the insoluble residue were found to contain idocrase. The insoluble residue, however, was analyzed and found to contain iron oxide, alumina, calcia and silica and these are allotted to idocrase, as is also about half of the magnesia. Calcite was not found in the ellestadite specimen and, because wilkeite and numerous other apatites contain CO_2, there is no reason for believing that the CO_2 reported is not a constituent of the ellestadite molecule.

The calculation of the charges shows a slight discrepancy, but this is not excessive when it is remembered that several of the factors for the positive ions are as great as five and six.

The various ions of the structure are relegated to the four different sorts of ionic positions of fluor-apatite as follows:

$$\begin{array}{l}
10\ \mathrm{Ca} = 9.92\ \mathrm{Ca} + 0.06\ \mathrm{Mg} + 0.02\ \mathrm{C} \\
\ \ 6\ \mathrm{P} = 0.44\ \mathrm{P} + 2.62\ \mathrm{S} + 2.82\ \mathrm{Si} + 0.12\ \mathrm{C} \\
\ \ 2\ \mathrm{F} = 0.30\ \mathrm{F} + 0.47\ \mathrm{Cl} + 0.51\ \mathrm{OH} + 0.72\ \mathrm{O} \\
24\ \mathrm{O} = 24\ \mathrm{O}\omega \\
\overline{} \\
42\ \ = \text{ionic positions of fluor-apatite.}
\end{array}$$

The ratio of the carbon in Ca-positions to carbon in P-positions is 0.02:0.12 which, peculiarly enough, is similar to the distribution found in the case of francolite (0.113:0.652) where there was, however, 3.36% of CO_2 instead of only 0.61% (6). Not only do both of the wilkeite specimens examined contain CO_2, but both of them contain halogens, as follows:

	D^7	$n_{\omega+\epsilon/2}$	$P_2O_5{}^7$	$SiO_2{}^7$	Cl^7	F^7	$CO_2{}^7$
Ellestadite, I	3.07	1.652	3.1	17.3	1.6	0.6	0.6
Wilkeite, II	3.12	1.648	14.4	11.2	0.8	0.9	*
Wilkeite, III	3.16	1.638	32.2	2.9	0.4	2.1	*
Fluor-apatite	3.18	1.632	41.3	—	0.1	3.7	0.5

* Present, but not determined.

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[7] These values have been reduced by one significant figure for simplicity. This has no bearing on the more exact values given elsewhere.

Because the methods used to determine the halogens are extremely reliable, there can be little doubt regarding the existence of the voelckerite molecule. Even if it were to be assumed that CO_3-groups can enter the structure in the F-positions, there would still be a deficiency which would require the assumption of the voelckerite molecule. Because CO_2 cannot enter the structure in this manner as has been shown (6) and because Bredig, Franck and Füldner (9) have obtained synthetic preparations containing 60–70% of this molecule, there can be no further doubt concerning its existence. These authors, however, found that pure oxy-apatite (voelckerite) cannot exist and this is probably to be explained on the basis of the hypothesis, advanced here, that the composition is not $Ca_{10}O(PO_4)_6$, but $(Ca, X)_{10}O_2(PO_4)_6$. The additional negative charges which arise through the introduction of an additional O-ion may be compensated by carbon substituting for calcium on the threefold axes, in which case the balanced formula becomes $(Ca_9C)O_2(PO_4)_6$. For structural reasons the formula $Ca_{10}O(PO_4)_6$ seems highly improbable.

A sulfate-apatite was reported by Brauns (10) from the Laacher See district. He states, however, that it was not possible to ascertain the true relationship of the SiO_2 to the other constituents.[8] Recalculation of Brauns' analysis suggests that part of the insoluble matter, of which there was 4.80%, was silica which replaced phosphorus in the structure. If this be true Brauns was dealing with wilkeite from a second locality, but this supposition requires further confirmation.

Summary and Conclusions

The apatite group is composed of a number of isomorphous series. The series apatite-wilkeite-ellestadite has been investigated in terms of both end-members and two intermediate members. Ellestadite has not been previously recognized, and a substance very close to this end-member was found to have the following properties:

Chemical composition: a calcium sulfate-silicate, containing halogens and minor amounts of CO_2 and P_2O_5.

Structure: space group C_{6h}^2, with $a_o = 9.53 \pm 0.01$Å, $c_o = 6.91 \pm 0.01$Å and $c/a = .7251$.

Optical properties: uniaxial, negative, $\epsilon = 1.650 \pm .002$, $\omega = 1.655 \pm .002$.

Physical properties: sp. gr. 3.068 (4°C.), cleavage and other properties essentially similar to apatite.

Locality: Crestmore, Riverside County, California.

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[8] "Aus dem Umstand, dass bei der Auflösung dieses Apatits eine zarte Haut von Kieselsäure in dem Umriss des aufgelösten Kristalls zurückbleibt, könnte man weiter schliessen, dass auch Kieselsäure als eine der Nebensäuren auftritt; diese Frage kann aber aus Mangel an Material nicht entschieden werden." (10, p. 89.)

Although ellestadite and wilkeite contain halogens and carbon dioxide, it is necessary to assume that they also contain the oxy-apatite molecule. A slightly modified formula for this molecule is suggested for structural reasons, and this is $(Ca, X)_{10}O_2(PO_4)_6$.

The almost complete replacement of phosphorus, one of the chief constituents of apatite, by sulfur and silicon without appreciably altering the structure is most interesting and has rather broad implications.

Carbon dioxide was found to play a dual rôle in its manner of entering the apatite structure, as has been previously found in the case of francolite. This and other features contribute to the great complexity of the isomorphism of the apatite group.

The structural formula of ellestadite and (with slight modification) of wilkeite is:

$$[Ca_6(F,Cl,O,OH)_2]\ [(S,Si,P,C)O_4]_6(Ca,C)_4$$

This formula indicates that two-fifths of the Ca-ions are located on threefold axes and can be replaced by carbon. Three-fifths of the Ca-ions are tied to F-, Cl- and O-ions or OH-groups, and cannot be replaced by carbon. All of the Ca-ions are tied to O-ions which are arranged in tetrahedral configurations with S-, Si-, P- or C-ions at their centers.

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THE NORMAL TRICLINIC SETTING: CORRECTION

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In a recent paper on the crystallography of axinite (1937 A) a unique setting was proposed for triclinic crystals and named the *normal setting*, since it was founded on principles and conventions which are now widely accepted. The normal setting was defined as the setting in which the geometrical elements refer to the cell given by the three shortest non-coplanar identity periods of the structural lattice, in the one orientation in which the axis *c*[001] is the axis of the main zone, the plane *c*(001) slopes to the front-right, and the axis *b*[010] is greater than the axis *a*[100].

The condition that the base shall slope to the front-right is most directly expressed by stating that the pole of (001) must lie in the first quadrant where its azimuth angle ϕ is between 0° and +90°. Alternatively, it seemed, the same condition was defined by stating that the direct axial angles α and β shall both be obtuse; and in several recent papers, by the writer and others who consulted him, these two modes of defining the normal attitude of the base were used indiscriminately in the belief that they were equivalent. The following tabulation gives the relevant angles for five triclinic species which have recently been described in the normal setting; in each case it will be seen that both the apparently equivalent rules are obeyed: ϕ_{001} positive, acute; α and β both obtuse.

	ϕ_{001}	$\nu(\phi_{100})$	α	β	
Axinite	89°23′	102°38′	91°51½′	98°04′	Peacock (1937 A)
Rosenbuschite	60 33	67 30	91 21	99 38½	Peacock (1937 B)
Gordonite	54 19½	102 49	109 27	110 57½	Pough (1937)
Babingtonite	56 39½	75 49½	91 31	93 51	Richmond (1937)
Römerite	87 24½	94 19½	91 17	100 30	Wolfe (1937)

While working on the crystallography of tarbuttite Mr. W. E. Richmond, Jr., found that the axial angle α is less than 90° when (001) lies in the first quadrant. This led to a reexamination of the geometrical relations involved, which clearly showed that under certain uncommon conditions α may be acute when the base slopes to the front-right. There are two cases, best seen in the stereographic projections (Figs. 1, 2), which give the poles of the axial planes, *a*(100), *b*(010), *c*(001), of a triclinic parallelepiped, the direct axial angles $\alpha\beta\gamma$, the polar axial angles $\lambda\mu\nu$, and the azimuth of the base ϕ_{001}; in both cases *c*(001) slopes to the front-right. In Fig. 1 $\nu(\phi_{100})$ is greater than ϕ_{001}; the zone-circle *ac* passes to the right of the centre and α is obtuse, as in the five examples given. In Fig. 2, however, $\nu(\phi_{100})$ is less than ϕ_{001}; the zone-circle *ac* passes to the left of the centre, and α is acute. Evidently there is also a special intermediate case, precisely realized in wollastonite (1935), in which $\phi_{100}=\phi_{001}$ and $\alpha=90°00'$. It is clear, therefore, that α is obtuse only when the azimuth of (100) is greater than that of (001), and that therefore the rule "α and β both obtuse" is not strictly equivalent to the rule "ϕ_{001} between 0° and +90°."

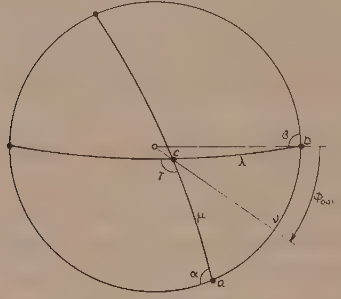

FIG. 1

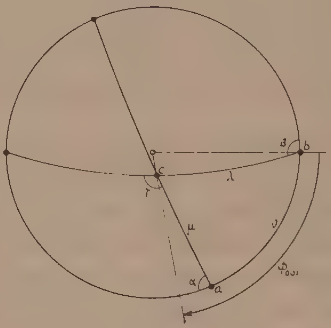

FIG. 2

In seeking a unique setting for triclinic crystals for determinative purposes Barker (1930, p. 13) gave the following rules to place the base in the conventional attitude: "(3) The zone-angle *abc* is taken less than 90°. (4) The great circle *ac* must traverse the projection to the right of the centre." These rules are exactly equivalent to "α and β both obtuse," as in our Fig. 1; they are not obeyed in Fig. 2 in which *c*(001) still lies in the first quadrant. If the normal setting and that of Barker rested on a common foundation it would be desirable to retain uniformity in the matter of the rule regarding the attitude of the basal plane. But such is not the case. Barker's method takes no account of the structural lattice, as determined by *x*-rays or by a comprehending consideration of the external geometry; it will therefore never be adopted as a general system of morphology, although it may yet serve its important purpose of providing a ready means of classifying and identifying chemical compounds from the angular relations of their crystal planes.

We propose, therefore, to retain the rule regarding the base in the form "ϕ_{001} lies between 0° and +90°," or its strict equivalent: "the angles *abc*(180°–β) and *bc*(λ) are both acute," and discard the rule: "α and β are both obtuse," which is frequently but not always equivalent to the first and second expressions.

The above correction in no way affects the singleness or propriety of the normal setting or its application in any of the published cases; it bears only on the wording of the rule which ensures the conventional attitude of the basal plane.

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——— (1937 A): *Am. Mineral.*, vol. **22**, pp. 588–620.

——— (1937 B): *Norsk Geol. Tidssk.*, vol. **17**, pp. 17–30.

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Richmond, W. E., Jr. (1937): *Am. Mineral.*, vol. **22**, pp. 630–642.

Wolfe, C. W. (1937): *Am. Mineral.*, vol. **22**, pp. 736–741.

THE STAUROLITE AREA OF PATRICK AND HENRY COUNTIES, VIRGINIA*

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Staurolites from Patrick County have attracted considerable attention for many years because of their tendency towards a cruciform type of twinning, and their use as watch charms and pendants for necklaces. A brief description of their location, mode of occurrence and uses, as well as of the artificial crosses has been recently given.[1]

The writer made field studies in the above named counties during the summer of 1936, mapping the extent of the staurolite-bearing and associated rocks, and followed this during the past fall and winter with a study of thin sections. This brief description gives the results of study on a region of Virginia which has received comparatively little attention up to the present time.

Staurolites occur intermittently in a rather narrow area, which extends from four miles below Stuart to Appomattox Court House. This paper will be confined to a description of the region occurring in Patrick and Henry Counties from which most of the collections have been made. Within this area there are two excellent collecting localities. One of them is at the southwestern extremity of the larger staurolite lens, located on state highway No. 631, four miles southwest of Stuart. The staurolite crystals here, while of the largest size observed within this area, occur embedded in the rock (see Fig. 1). The other locality for collecting is at the northeastern extremity of the same lens, on the border of Patrick and Henry Counties, twenty miles by road northeast of Stuart, or thirteen miles by air line. In this last named locality there is an abundance of loose crystals lying upon the surface.

The staurolites in these two counties occur in two belts approximately parallel to each other. One belt begins at a point four miles southwest of Stuart, and extends approximately in a N. 50° E. direction for a distance of nineteen miles. The other belt begins at a point nine miles northeast of Stuart, and one-half mile southeast of the first belt, and extends to and beyond the Franklin County line. Both belts are roughly lenticular in shape and have a maximum width of two and one-half miles.

The three principal rocks associated with the staurolites are a biotite chlorite schist, a sericite staurolite schist, and an iron stained quartz mica schist. The rocks form a portion of the Wissahickon formation where the Martic overthrust block over-rides the Lynchburg gneiss. They form a sharp contact with the Lynchburg gneiss along their northwestern boundary and grade into less metamorphosed Wissahickon on the southeast. These rocks appear to be products of retrogressive metamorphism and may be termed phyllonites.

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* Published by permission of Virginia Geological Survey.

[1] Roberts, Joseph K., Virginia staurolites as gems: *Am. Mineral.*, vol. **19**, pp. 549–552, 1934.

The staurolite crystals occur as reddish brown idioblasts, one tenth of an inch up to one and one-half inches in length, in each of the three rock types, and are altered wholly or in part to sericite and chlorite. They contain numerous inclusions of small garnets, which weather out giving the appearance of pits in the staurolite crystals. The staurolites seem to be most numerous at the ends of the lenticular belts.

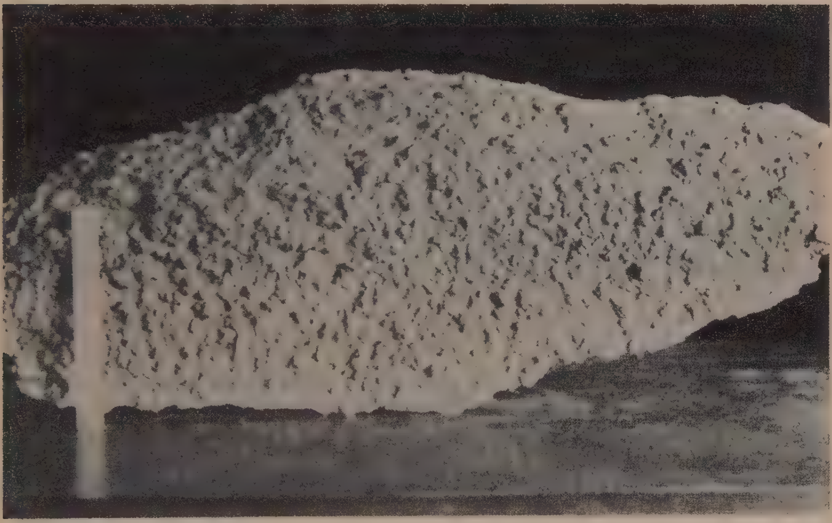

FIG. 1. View of a slab of sericite schist, showing staurolite crystals. Scale of 6 inches to left.

The staurolites are generally twinned, although not a few occur as simple crystals with usually only a prism and basal pinacoid developed. Occasionally other crystal forms appear, particularly macro- and brachypinacoids and domes. No bipyramids were observed. Penetration twins according to two laws are common, yielding X-shaped and cross- or plus-shaped twins. A careful study of many crystals has shown that 75% are twinned according to the first law. In this type of twinning, the twin plane $Z(232)$ crosses at angles varying from 35 to 60 degrees. The greater number are nearer the latter figure. Many of them show multiple twinning, a given crystal being penetrated by two or more crystals. Aggregates containing a number of the X-shaped twins, as well as simple crystals, are of frequent occurrence.

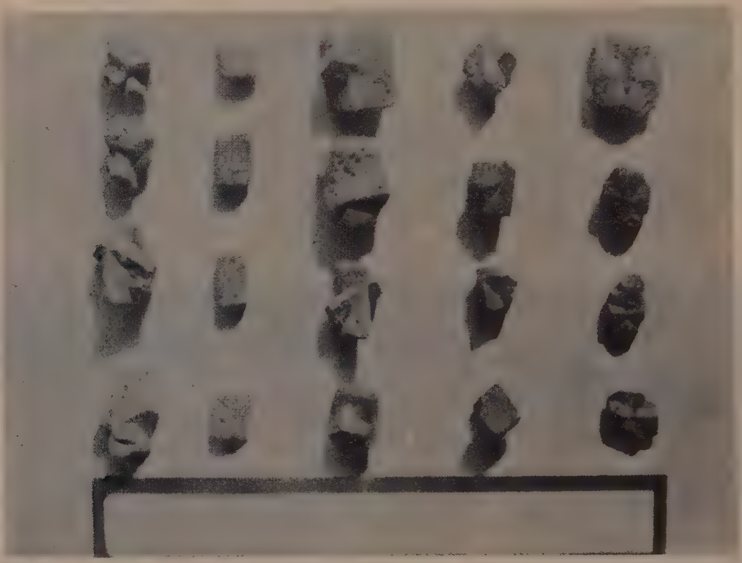

FIG. 2. Various types of staurolites found in Henry and Patrick Counties, Va., showing single crystals, aggregates, X-shaped and +-shaped twins.

Cruciform crystals crossing nearly at right angles make up less than 5% of the total number observed. Excellent specimens are relatively rare. Here the twin plane is generally referred to as $\{032\}$. The crystal forms observed on twins of this type, as well as those on the X-shaped twins, are the same as those occurring on the simple crystals.

The staurolites are greenish gray to reddish brown in color. Much of the brown and red colors result from limonite stains. The brown color observed in crystals on the market is not characteristic of the natural crystal. Many, no doubt, have been artificially colored. Practically all specimens show numerous pits which have resulted from the dropping out of inclusions. Where these inclusions are still present they are usually garnets. The greenish color can be traced to the alteration products, chlorite and sericite, as is shown under the microscope.

A study of thirteen thin sections of staurolite has revealed the following microscopic features: cleavage varies from weak to strong, dependent upon the degree of alteration and number of inclusions. The direction of cleavage is parallel to {010}. The crystals exhibit a marked pleochroism, the color being orange yellow in the fresher specimens and grading down to pale yellow in the more altered ones. The direction of slowest vibration is parallel to the *c* axis, and the character of the pleochroism may be indicated as follows: Along the *c* axis, light yellow or orange yellow; parallel to the *a* and *b* axes, colorless or pale yellow. The optic sign of the mineral is positive.

All the sections of crystals from Patrick and Henry Counties contain inclusions of such quantity that they compose approximately 50% of the total mass. They are, in order of abundance, quartz, garnet, graphite (?), muscovite, biotite, tourmaline, and magnetite.

The small anhedral grains of quartz (average size less than 0.1 mm. in diameter) are by far the most numerous of the inclusions. In places they almost obliterate the staurolite by their abundance. Garnet (almandite) crystals, usually broken, vary from 0.2 to 1.5 mm. in diameter. The garnets in turn contain inclusions of quartz, muscovite, and a black opaque material. This ragged, black, opaque material, in the form of needles, varies up to 0.3 mm. in length and is of approximately parallel orientation; it is abundant in all thin sections. These needles were tentatively identified as graphite. Penfield and Pratt[2] have shown that the regularly arranged opaque material in the staurolites from Lisbon, New Hampshire, is carbonaceous material. Muscovite occurs sparingly in small plates around the edges of the staurolite crystals, and occasionally as small needles oriented at random through the crystals. On the other hand, the few plates of biotite observed were always within the staurolite. Tourmaline is quite abundant as an accessory mineral, occurring in small pleochroic crystals. Magnetite is scattered throughout the slides in masses of irregular shape and size.

Twinning is to be observed in nine of the thirteen slides examined. In only a few cases could the twinning be recognized in thin sections without crossed nicols. The majority of the sections of the mineral were cut parallel to *c* axis on one crystal, and perpendicular to *c* on the penetrating crystal, so in the unaltered twins, the difference in the degree of pleochroism makes recognition possible. Contrary to the assumption suggested by the megascopic appearance, not one of the twins examined microscopically showed one crystal penetrating entirely through the other. It appears, after a cursory examination, as though each side of the penetrating crystal were a separate entity, because their terminations inside the penetrated crystal are always wedge-shaped, and in most cases stop short of the center of the other crystal. In only one instance were the two wedges pointing directly towards each other (see Fig. 3). Nevertheless, careful megascopic examinations show such a genetic relationship between the two sides of the penetrating crystal as to preclude the possibility of it being two separate entities. The penetrating and penetrated crystals probably grew simultaneously, and since the penetrated one is usually the larger, it may have absorbed that part of the other which was within its boundaries and used the material to further its own growth. Another possibility is that the twin in some cases may not have been cut directly through the center. This would expose only the top of the penetrating crystal, provided the section was cut parallel to the *c* axis of both crystals. This would give the wedge-shaped appearance. However, since the majority of the slides used were cut parallel to the *c* axis of one crystal and normal to the *c* axis of the other, if the penetrating crystal extended entirely through the other, it certainly would have been observed.

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[2] Penfield, S. L. and Pratt, J. H., On the chemical composition of staurolite and the regular arrangement of its carbonaceous inclusions: *Am. Jour. Sci.*, vol. **47**, pp. 81–89. 1894.

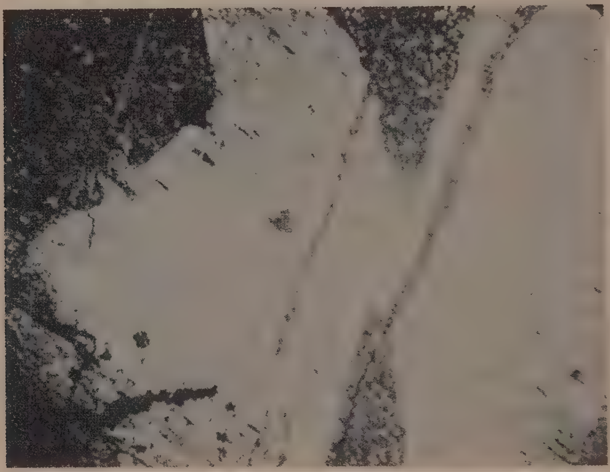

Fig. 3. View showing penetration twins in a staurolite crystal, where points are approximately diametrically opposed. X-Nicols, ×20 diameters.

The staurolites are almost universally altered. In many cases the alteration is complete, the former existence of the individual is indicated only by its crystallographic outline. The alteration products are sericite, chlorite, and limonite. The alteration to sericite generally begins along fractures and cleavage planes and works outwards, until in some cases, the entire crystal is involved. In many of the intermediate stages a crisscross pattern results from alteration along intersecting planes. The size of the individual flakes of sericite vary, being larger in the middle of the altered areas and decreasing in size outwards. These altered areas of sericite are usually stained with limonite. Limonite also occurs as alteration rims around most of the garnets.

The alteration of staurolite to chlorite, while not as abundant as its alteration to sericite, is not infrequent. The variety is usually pennine, although sometimes clinochlore is present. Various stages of alteration can be recognized by the pale yellow color of the staurolite, and the light green color of the pennine. In some cases the alteration to pennine is complete with only the crystallographic outline of the staurolite remaining. Chlorite also occurs as an alteration product of garnet and biotite. Some of the chlorite exhibits pleochroic halos around inclusions of quartz. It appears as though this quartz is also secondary, having filled spaces formerly occupied by some other radio-active mineral. In other instances quartz fills spaces originally occupied by garnets.

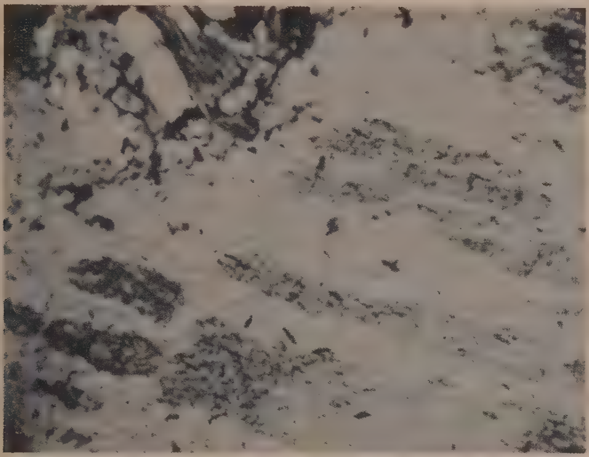

FIG. 4. Staurolite showing characteristically weathered condition, light areas are sericite and dark areas are staurolite remnants. X-Nicols, ×20 Diameters.

There is evidence from the biotite-staurolite-garnet association that the rocks were formed under conditions of static or load metamorphism in the mesozone of von Grubenmann, and the amphibolite facies of Eskola. The great number of inclusions of quartz, biotite, muscovite, garnet, tourmaline, and zircon in the staurolite indicates that it was one of the last minerals to form. Krishman[3] finds in an occurrence of staurolite in India that the largest and best formed crystals occur in close proximity to igneous injections, and further, that basic sills exert more influence than granitic bosses. He believes that although injections did not contribute any material, they have been of help by increasing the mobility of the molecules during metamorphism by increasing the temperature.

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[3] Krishman, M. S., On the occurrence and distribution of staurolite in Gangpur State, Bilear and Orissa, India: *Indian Sci. Congr.*, 20th (Patna), p. 345, 1933.

It is of particular significance that to the writer's knowledge, in all reports of diapthoritic areas accompanying major overthrusts, mention is made of staurolite. The staurolites of India as well as those in Patrick and Henry Counties, Virginia, occur in such an area. The sericite-chlorite association, characteristic of the epizone of von Grubenmann, and the green schist facies of Eskola of rocks that still contain some of the mineral characteristics of the mesozone is highly indicative of retrogressive metamorphism. It appears as though the larger staurolitic areas are, in the majority of cases, exposed only by overthrusts. Of significance also is the highly altered condition of staurolite when exposed in this manner. A comparison of staurolite from Patrick and Henry belts with specimens from an isolated occurrence to the west, near Galax, Virginia, collected by Dr. W. T. Schaller of the U. S. Geological Survey, showed the former to be so much more altered and to have incorporated so much more foreign material that thin sections of the weathered and fresh staurolite in thin sections could very easily be mistaken for two different minerals. Dr. Schaller kindly gave some of the fresh staurolites to the writer for comparison with specimens from Patrick and Henry Counties. Evidently the fault plane of the Martic overthrust block allowed free passage for ascending hot waters. All of the rocks in proximity to the fault plane, as well as the staurolites themselves, show mineral associations highly suggestive of hydrothermal alteration. The presence of epidotized meta-gabbro dikes, pyrite, limonite, sericite, chlorite, secondary quartz, and the universal alteration of the staurolite are all indications of this condition.

NOTES AND NEWS

AN OCCURRENCE OF DIASPORE IN QUARTZITE

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A study of specimens of the Sioux quartzite from several localities in southwestern Minnesota and southeastern S. Dakota shows that diaspore is an abundant and characteristic mineral of at least large portions of the formation. Since diaspore occurs most commonly in association with corundum and emery[1] or in residual clays[2] and bauxites, its occurrence in a quartzite is believed worthy of note. No similar occurrence of diaspore is known.

The Sioux quartzite (Algonkian) outcrops in portions of southwestern Minnesota and in neighboring parts of Iowa and South Dakota. The formation is of great thickness.[3] Most of it is well cemented but parts of the formation are porous and contain a small amount of cement.[4] There is no evidence that the Sioux quartzite was ever subjected to deep burial or to high temperature metamorphism. The formation was probably submerged during a portion of Cretaceous time because Cretaceous deposits overlie the quartzite in many localities.

Thin sections of all available specimens of the quartzite were examined. They are very similar and show that all the specimens contain diaspore. The specimens from Pipestone, Minnesota, were taken from positions stratigraphically higher than the well known "pipestone" or catlinite layer[5] which forms the basal portion of the outcrop.

The quartzite from Pipestone shows secondary growth, but there is little evidence of dynamic metamorphism. The outlines of the original quartz grains are for the most part distinct, indicating little recrystallization. Under crossed nicols the grains extinguish evenly and very few grains show any evidence of strain. A polished section shows clear rounded quartz grains in a cloudy matrix that, except for the diaspore, which acts partially as a cement, is composed of silica. The rock is thoroughly cemented.

The diaspore (see Fig. 1) forms irregular masses between the original sand grains of the quartzite, and subhedral and euhedral grains up to

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[1] Dana, E. S., *Descriptive Mineralogy*, New York, John Wiley and Sons, 1892, p. 247.

[2] Allen, Victor T., Mineral composition and origin of Missouri flint and diaspore clays: *Missouri Geol. Survey and Water Resources, 58th Biennial Report*, Appendix 4, **1935.**

[3] Rothrock, E. P., and Newcomb, R. V., Sand and gravel deposits of Minnehaha County, S. Dakota: *Geol. and Nat. History Survey, Circular* **26,** p. 9, 1926.

[4] Winchell, N. H., *Geology of Minnesota*, Vol. **I** of the Final Report, **1884,** p. 542.

[5] Winchell, N. H., *op. cit.*, p. 540.

.35 mm. in diameter. It constitutes over 3 per cent by weight of the quartzite, as determined by heavy liquid separation of the crushed quartzite grains. In thin section the diaspore is colorless, but concentrates from the crushed quartzite have a distinct pinkish color. The masses of diaspore are not aggregates but each mass has optical continuity. The mineral liberates water in a closed tube Qualitative chemical tests indicate abundance of aluminum. The refractive indices are: $\alpha=1.700$, $\beta=1.720$, $\gamma=1.752$ (all $\pm.003$). Using these indices the calculated $2V=83°$, approximately. The identification was kindly confirmed by Dr. J. W. Gruner, using an x-ray diffraction pattern.

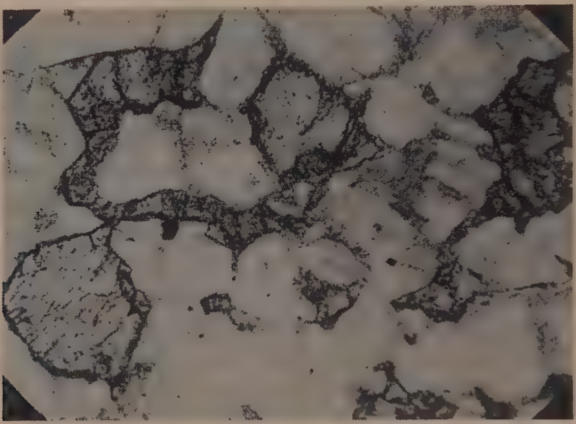

FIG. 1. Photomicrograph of a thin section of the Sioux quartzite from Pipestone, Minn. The mineral with high relief is diaspore. Other material is quartz. Plain light (×60).

Associated with the diaspore in the quartzite are rutile and iron oxides. The rutile occurs as euhedral crystals, some geniculate twins, and as very small irregular specks. Usually the rutile, which is rather abundant, lies between the original quartz grains but an occasional crystal penetrates a quartz grain. The iron oxides are probably largely responsible for the distinct reddish color of the rock. In thin section these oxides appear to be concentrated in the interstitial spaces and on the borders of the quartz grains.

Detailed field and laboratory study might definitely establish the genesis of the diaspore. From the evidence at hand, however, several possibilities may be mentioned. The diaspore could hardly be detrital. It is equally unlikely that it could have been formed at high temperatures, not only because the quartzite formation itself lacks evidence of high temperature metamorphism, but also because at high temperatures the alumina would probably have reacted with the silica present to form an aluminum silicate.

Perhaps the most likely hypothesis is that the diaspore was formed from differential leaching by meteoric waters. The leached material might have been any aluminous silicate or silicates originally present in the formation or, possibly, silicates which were introduced in colloidal solutions. Supporting the leaching hypothesis is the fact that feldspars, clay minerals and other silicates are almost if not quite lacking in the specimens studied. This evidence, however, is only of negative value as the original mineral composition of the formation is unknown. The considerable amount of rutile also lends support to the idea of leaching. The rutile very likely was derived by alteration of ilmenite or other titanium-bearing minerals. Titanium is recognized as a concentration product and is usually found in residual clays and bauxites.[6]

Whatever may be the genesis of the diaspore it is certain that the agencies of metamorphism have had a very long time in which to effect their alterations. The formation is pre-Cambrian and, as noted above, portions of it are still porous and poorly cemented. The cementation of the quartzitic portions of the rock seems likely to have followed the formation of the diaspore although secondary growth of the quartz and leaching of the silicates might have been contemporaneous. In fact the silica leached from the silicate minerals may have contributed to the cementing material.

The writer has already begun a detailed study of all phases of the Sioux quartzite.

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[6] Clarke, F. W., *The Data of Geochemistry, U. S. Geol. Surv., Bull.* **770**, 1924, p. 503.

AN OCCURRENCE OF DETRITAL AUTHIGENIC FELDSPAR

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INTRODUCTION

A sample of fine sand collected from the bottom of a 27 foot water well in a lacustrine plain covered by the Flint moraine, near Mt. Morris, Michigan, SW $\frac{1}{4}$, NW $\frac{1}{4}$, Section 6, T. 8 N., R. 7 E., Genesee Township, has yielded an interesting suite of minerals, including detrital authigenic feldspar. The finding of such feldspar in the drift introduces the problem of the source of the authigenic grains.

Authigenic feldspars have been recorded as a constituent of certain arenaceous and calcareous rocks. Boswell[1] lists 50 references, only two of which mention authigenic feldspars in North America. Daly[2] noted the presence of what we now call authigenic orthoclase in a dolomite in Alberta. He was the first to make a study of such an occurrence in North America.[3] Authigenic grains have been observed also in certain calcareous rocks in North Carolina.[4] Singewald and Milton[5] noted authigenic feldspars in New York. Derry[6] recorded the presence of probable authigenic feldspars, microcline and albite and possibly orthoclase, in Ontario. Goldich[7] reported such feldspars from Minnesota, and mentioned occurrences in Wisconsin and Missouri. He states,[8] "The nuclei of the great majority of the grains seem to be triclinic potash feldspar, microcline. The marginal growths, however, appear to be more nearly the monoclinic variety, orthoclase . . . ." Tester and Atwater[9] discussed the occurrence of authigenic feldspars in sediments, noting them in

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[1] Boswell, P. G. H., *On the Mineralogy of Sedimentary Rocks*, Thomas Murby and Co. 393 pp., 1933.

[2] Daly, R. A., Geology of the North American Cordillera at the forty-ninth parallel: *Canada Geol. Surv., Mem.* **38,** Part I, pp. 52–54, 1912.

[3] Daly, R. A., Low-temperature formation of alkaline feldspars in limestone: *Proc. Nat. Acad. Sci.*, vol. **3,** pp. 659–665, 1917.

[4] Loughlin, G. F., Berry, E. W., and Cushman, J. A., Limestones and marls of North Carolina: *North Carolina Geol. and Econ. Surv., Bull.* **28,** principally pp. 20, 53 and 58, 1921.

[5] Singewald, J. T., Jr., and Milton, Charles, Authigenic feldspar in limestone at Glens Falls, New York: *Bull. Geol. Soc. Amer.*, vol. **40,** pp. 463–468, 1929.

[6] Derry, D. R., Heavy minerals of the Ordovician sediments of Ontario: *Jour. Sed. Pet.*, vol. **4,** No. 2, pp. 85–86, 1934.

[7] Goldich, S. S., Authigenic feldspar in sandstones of southeastern Minnesota: *Jour. Sed. Pet.*, vol. **4,** No. 2, pp. 89–95, 1934.

[8] *Op. cit.*, pp. 90–91.

[9] Tester, A. C., and Atwater, G. I., The occurrence of authigenic feldspars in sediments: *Jour. Sed. Pet.*, vol. **4,** No. 1, pp. 23–31, 1934.

Iowa, Kansas, Minnesota, Wisconsin, and New York. They remark,[10] "Authigenic feldspar can be used to differentiate horizons as it frequently occurs as a 'flood' mineral in the lighter fractions of a mineral separation." Atwater and Clement[11] described such feldspars from Wisconsin and Minnesota. Thiel[12] reported occurrences in Wisconsin, Minnesota, Illinois, Missouri, and Arkansas. Stringham[13] has noted their presence in Utah and Tyler[14] recorded their occurrence in Wisconsin. Gruner[15] has noted small particles of feldspar which are probably authigenic in certain Minnesota rocks.

Method of Study

The sand was separated into two fractions using acetylene tetrabromide (G. = 2.95) which were then washed in benzene and dried in beakers on a hot plate. The heavy minerals were mounted in Canada balsam. The light fraction was immersed in a solution of acetylene tetrabromide and benzene whose specific gravity was such that a fragment of microcline would float and a chip of quartz would settle. A very satisfactory separation of the feldspars and quartz was obtained. The two fractions, feldspars and quartz, were washed in benzene and dried on a hot plate, after which the specimens were bottled in suitably labeled vials. The grains were examined microscopically in 1.54 index liquid, without a cover glass. Authigenic grains were separated from the other feldspars with a needle and washed in a drop of benzene in a small watch glass. Individual grains, taken up with a needle, were then pressed into warmed dry Canada balsam, the slide reheated, and the cover glass added.

Seventy slides of feldspar fractions were examined from which 14 grains of detrital authigenic feldspar were removed, and 12 mounted. Eight slides of heavy concentrates were studied.

Minerals in the Sand

The following minerals have been identified in the glacial sand: Actinolite, albite, apatite (well-rounded to slightly rounded prismatic grains), augite (light green), titaniferous augite (?), biotite, brookite, rhombohedral carbonate, chalcopyrite, chert (angular to well-rounded), enstatite, epidote, feldspar (unidentified species altered to kaolin and sericite), garnet (colorless, pink, and darker reddish shades), hematite, green hornblende, hypersthene (rounded to prismatic grains, exhibiting strong pleochroism), ilmenite, kyanite, leucoxene, limonite, magnetite, microcline (as nuclei about which another feldspar has formed; also, as well-rounded to angular grains, the well-rounded type being the most common), muscovite, orthoclase, quartz (well-rounded to angular; some grains doubly terminated; often containing inclusions of rutile needles, tourmaline and apatite crystals), pyrite, rutile, sphene (light to dark brown; often rounded), staurolite, brown tourmaline (well-rounded to prismatic grains), blue tourmaline, zircon (rounded to prismatic grains), and zoisite.

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[10] *Op. cit.*, p. 27.

[11] Atwater, G. I., and Clement, G. M., Pre-Cambrian and Cambrian relations in the Upper Mississippi Valley: *Bull. Geol. Soc. Am.*, vol. **46**, p. 1677, 1935.

[12] Thiel, G. A., Sedimentary and petrographic analysis of the St. Peter Sandstone: *Bull. Geol. Soc. Am.*, vol. **46**, pp. 589–592, 1935.

[13] Stringham, Bronson, An occurrence of feldspars replacing fossils (Abs.): *Am. Mineral.*, vol. **21**, No. 3, p. 200, 1936.

[14] Tyler, S. A., Heavy minerals of the St. Peter Sandstone in Wisconsin: *Jour. Sed. Pet.*, vol. **6**, No. 2, p. 82, 1936.

[15] Gruner, J. W., Unusually high feldspar content of the Glenwood formation (Abs.): *Am. Mineral.*, vol. **22**, No. 3, p. 212, 1937.

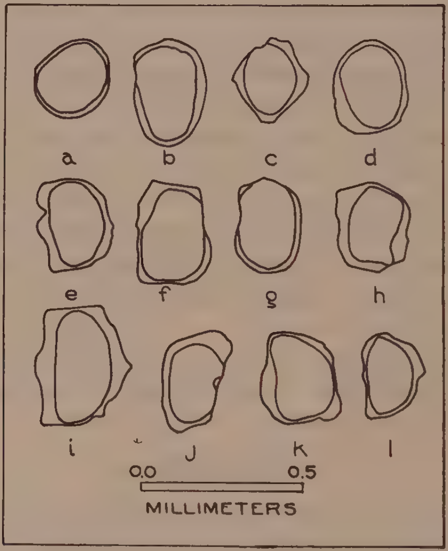

FIG. 1. Sketches of authigenic feldspar.

AUTHIGENIC FELDSPAR

Fourteen grains of slightly altered authigenic feldspar were noted in the slides studied, and twelve of these were examined microscopically. Figure 1 illustrates the shapes and sizes of the grains. About a nucleus of feldspar another feldspar whose optical character and orientation is other than that of the central grain has been formed as a marginal growth. Measurements were made with a recording micrometer of the long and short diameters of the nuclei, and of the maximum widths of the marginal growths. The average long diameter of the nuclei is 0.272 mm., that of the short diameter, 0.183 mm., and the average of the maximum widths of the rims, 0.046 mm. The maximum long diameter of the nuclei is 0.350 mm. and the minimum, 0.225 mm. The maximum short diameter of the nuclei is 0.215 mm. and the minimum, 0.155 mm.

Grains *a*, *b*, *c*, *d*, *e*, and *g* have nuclei of microcline showing excellent quadrille structure, and yield poor interference figures. The character of the nuclei is biaxial negative. The majority of the other feldspar grains exhibit indistinct twinning lamellae or none at all. The marginal growths of grains *f*, *i*, *j*, *k*, and *l* are considered to be adularia. Good biaxial negative interference figures with very small optical angles were obtained from these specimens. The composition of the rims of the other grains is probably potash feldspar, although sufficient data for exact determinations were not possible.

Probable Source of the Authigenic Feldspar

The authigenic feldspar is found in a lacustrine plain which is covered by the Flint moraine, laid down by the Saginaw ice lobe of the Wisconsin ice sheet. Taking into consideration the direction of ice movement the location of the source of this feldspar is limited to a certain extent. It is possible that the feldspar source is in Ontario, but because of its slightly altered condition and relatively abundant occurrence in the sediment the source in Michigan rocks seems more likely. The strata over which this lobe passed include the common sedimentary rock types, varying in age from Devonian through Pennsylvanian. A study of residues of certain rocks from the strata of the Paleozoic formations is contemplated with the expectation that the source of the authigenic grains may be found.

Acknowledgments

The author gratefully acknowledges the kind assistance of Professor Stanard G. Bergquist in this preliminary investigation. Professor Walter F. Hunt checked the identifications of two of the minerals of the heavy concentrates.

NOMINATIONS FOR OFFICERS OF THE MINERALOGICAL SOCIETY OF AMERICA FOR 1938

The Council has nominated the following for officers of *The Mineralogical Society of America* for the year 1938:

PRESIDENT: Ellis Thomson, University of Toronto, Toronto, Canada.

VICE-PRESIDENT: Kenneth K. Landes, University of Kansas, Lawrence Kansas.

SECRETARY: Paul F. Kerr, Columbia University, New York, New York.

TREASURER: Waldemar T. Schaller, United States Geological Survey, Washington, D.C.

EDITOR: Walter F. Hunt, University of Michigan, Ann Arbor, Michigan.

COUNCILLOR (1938–1941): R. C. Emmons, University of Wisconsin, Madison, Wisconsin.

The eighteenth annual meeting of the Society will be held December 28–30, 1937, at the Hotel Washington, Washington, D.C.

A preliminary list of the titles of papers to be presented before the Society at its annual meeting will be published in the December issue of *The American Mineralogist*. Titles of papers should be in the hands of the Secretary by *November 8th*.

Printed programs containing a schedule of the papers to be presented at the annual meeting, together with the abstracts of the papers, will be mailed to all members of the Society with the December issue of the *Journal*. Abstracts for this program, *in duplicate*, should be in the hands of the Secretary by *November 20th*. Abstract blanks may be obtained from the Secretary on request.

PAUL F. KERR, *Secretary*

BOOK REVIEWS

A DESCRIPTIVE PETROGRAPHY OF THE IGNEOUS ROCKS, VOLUME III—THE INTERMEDIATE ROCKS. ALBERT JOHANNSEN, pp. 360+xiv. The University of Chicago Press, Chicago, **1937,** price $4.50.

This volume describes the rocks from syenite to gabbro; or in Shand's classification the saturated rocks, together with the rocks that are oversaturated with respect to the bivalent elements excluding the ultramafic rocks; or families 9 to 12 of Johannsen which include those rocks with essential feldspar that lack essential quartz and feldspathoids.

This volume follows the same plan as volume II and it maintains the same high quality. The statements made by the reviewer on the second volume[1] apply to the third volume.

The historical sketches showing the origin and development of our rock names, the changes in meaning and nomenclature with time, and the differences in usage at the present time by different nations or groups are valuable and show the author's scholarly knowledge of the literature, old and new. The numerous photographs of petrographers, the microphotographs and photographs of rocks, and the many chemical analyses and modes are of great value.

The reviewer is shocked at the frequent use of acid and basic for the plagioclases and rocks. Why not use sodic and calcic or Johannsen's sodiclase and calciclase for the plagioclase and the specific term that happens to be appropriate for the rock, such as silicic or mafic? In quoting Daly, the author nearly always refers to old publications of Daly, mostly of 1914 or older, while much new data are given by Daly in "Igneous Rocks and the Depths of the Earth," published in 1933.

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[1] Larsen, E. S., *Am. Mineral.*, vol. **18,** p. 311, 1933.

Following Johannsen's classification, the reviewer would transfer the tridymite trachytes of pages 78 and 79 to the rhyolites.

"Number three! exclaimed Rose. There is but one other." Quoted from Johannsen's title page. Petrographers look forward to the publication of the final volume of this scholarly work.

Esper S. Larsen

SILICATE ANALYSIS by A. W. Groves, with a foreword by A. Holmes. 230 pages. Thomas Murby & Co., 1, Fleet Lane, E.C. 4, London. **1937.** Price 12 s. 6 d.

Practically all previous texts on silicate analysis have been written by chemists and designed for those primarily engaged in chemical analysis. The writer of the present book is not only an accomplished chemist but also an able petrologist and is well qualified, therefore, to present some of the problems in the border field of geochemistry. As a result a considerable amount of valuable information on mineralogy and petrology is included, and thus the text departs from those restricting their scope to the determinations of the individual constituents. It is the hope of the author that any mineralogist or geologist with some training in analytical chemistry will be able to follow the instructions given and make, in many instances, his own determinations. In order that this might be done more readily, the procedures or methods are printed in bold face type while the theoretical discussions and general considerations are printed in ordinary type.

As this book is a manual for geologists as well as chemists, we find that aside from chapters on the normal and special methods for the determination of the various constituents, there are special chapters on technological applications, occurrence of the various elements, and a discussion on computations as a check on the accuracy of chemical analyses.

The book, because of its wide scope of information and the present interest in the chemical phases as applied to mineralogy and geology, should appeal to many scientific workers and no doubt will receive an enthusiastic reception.

W. F. H.

J. C. POGGENDORFF'S BIOGRAPHISCH-LITERARISCHES HANDWÖRTERBUCH FÜR MATHEMATIK, ASTRONOMIE, PHYSIK MIT GEOPHYSIK, CHEMIE, KRISTALLOGRAPHIE UND VERWANDTE WISSENGEBIETE. Band VI: 1923–1931. Part II (F–K), pp. 697–1438. Verlag Chemie, G. M. B. H., Berlin, **1937.** Price for each part is RM 85 (paper cover); if ordered in advance RM 76.50. Foreign orders 25% off.

As indicated in a previous review (*Am. Mineral,*. vol. **21,** p. 535), vol. VI of this comprehensive work deals with the period from 1923 to 1931. Part I (A–E) was issued last fall and Part II, which has just appeared, covers the names of scientists with letters ranging from F–K. Part III (L–R) and Part IV (S–Z) are in preparation. It is the expectation that Part III will appear in the fall of 1937 and Part IV in 1938.

This manual contains complete data relative to the lives and contributions of scientists in the fields listed in the title of the book. In its preparation 3,500 periodicals are being carefully abstracted and when the work is complete it will contain the names of approximately 10,000 workers of all nations. An excellent reference work for laboratories and libraries.

W. F. H.

ATOMIC STRUCTURE OF MINERALS. W. L. BRAGG. xiii+292 pages, 144 figs. Cornell University Press, Ithaca, New York, 1937. Price $3.75.

Professor W. L. Bragg was the George Fisher Baker Non-resident Lecturer in Chemistry at Cornell University in 1934. It is customary for the lectures to be printed in book form. However, since much of the material of these lectures was covered by a previous book —"The Crystalline State," Professor Bragg chose to make the present book a review of the work that has been done in investigating the structures of minerals. It is not a book of *x*-ray methods. There is a brief discussion of symmetry and space group nomenclature, of ionic radii, coordination, complex ions, and isomorphous replacement. The major portion consists of a systematic discussion of mineral structures, including all those reported up to the end of 1936. It brings together material which has been published in many different journals. Not only is this a matter of great convenience, but the discussions of the structures and their relationships will prove to be of great interest to mineralogists, whether they are crystal structure experts or not.

L. S. RAMSDELL